

# Optimization of enzymatic hydrolysis of leather waste

DAGMAR JANACOVA<sup>1</sup>, KAREL KOLOMAZNIK<sup>1</sup>, PAVEL MOKREJS<sup>2</sup>, VLADIMIR VASEK<sup>1</sup>

Tomas Bata University  
<sup>1</sup>Faculty of Applied Informatics  
<sup>2</sup>Faculty of Technology Zlin  
 Mostni5139, 760 01 Zlin  
 CZECH REPUBLIC

**Abstract:** - In this paper there is described control system for the new technology, which allows by the help of enzymatic hydrolysis to process the chromium tannery wastes. The both technology and control system were created in the Department of Automatic Control on Faculty of Technology in UTB Zlin

**Key-Words:** - Mathematic modelling, automatic control, enzymatic hydrolysis, tanning process

## 1 Introduction

Enzymatic hydrolysis presents 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 °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.

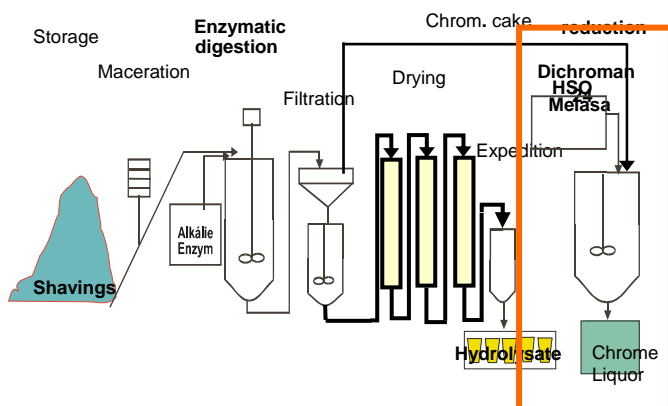


Fig.1. Scheme of enzymatic hydrolysis process

In order to successfully operate a full scale enzymatic hydrolysis of chrome containing wastes, the following tasks need to be fulfilled:

Estimate the investment and operational expenses  
 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
- the applications of the protein products.

It proceeds from the widest manufacture of tanning liquids, which are derived from chromium sulphuric acids. Reduction of hexavalent chrome into cubed raw sugar is accomplished by masking organic acids which are a by-product of the oxidation of sugar, which is advantageous particularly during two-bath tanning technology. Our technology of manufacture of tanning liquid rests in dosage suspension of filtration cakes to chromium sulphuric acid or the reverse, which arrives partly to the reduction of hexavalent chrome protein contained in the filtration cake partly to the dilution of chromium hydroxide. The result is a saving of dichromate and raw sugar. The reaction is exo-thermal and for this reason we have conducted a mathematic simulation of timed course of temperature in the mix of the chemical reactor, which is necessary for the successful control of the equipment for diluting reaction.

## 2 Recycling technology for chrome sludge

A large part of the works dealing with wastes of the leather industry, except for USDA publications<sup>26</sup>, does not go into particulars about how to cope with chrome sludge after dechromation of tanned wastes. As if chrome sludge so formed was automatically assumed to be simply used for producing recycled tanning salt. Even though the balance of chromium in chrome-tanned wastes and of necessary tanning salt is very favorable for recycling in the tanning industry, the actual situation is different. Although we quite correctly feel and hope that the issue of recycling

chromium into the tanning industry should be worked on or at least supported by manufacturers of chromic chemicals in the first place, we studied both the drawbacks of such recycling and applications in other fields

Producing recycled tanning salt

A typical composition of chrome cake we produce is presented in following table.

Table. Filter cake composition

| Oxide                          | Mass % | Mass % - after ignition |
|--------------------------------|--------|-------------------------|
| Na <sub>2</sub> O              | 0,42   | 1,35                    |
| MgO                            | 6,40   | 20,52                   |
| Al <sub>2</sub> O <sub>3</sub> | 0,40   | 2,85                    |
| SiO <sub>2</sub>               | 0,89   | 2,85                    |
| P <sub>2</sub> O <sub>5</sub>  | 0,12   | 0,38                    |
| SO <sub>3</sub>                | 1,50   | 4,81                    |
| CaO                            | 2,50   | 8,02                    |
| Cl                             | 0,33   | 1,06                    |
| Cr <sub>2</sub> O <sub>3</sub> | 15,90  | 50,97                   |
| MnO                            | 0,13   | 0,42                    |
| Fe <sub>2</sub> O <sub>3</sub> | 2,60   | 8,34                    |
| Ignition loss                  | 68,81  | ---                     |

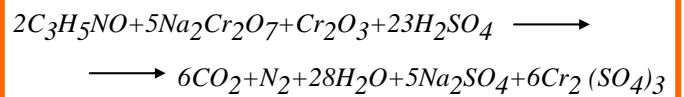
Under the term indirect technology we mean producing chromate by oxidation with air or oxygen in an alkaline medium. The method offering itself here is the processing of chrome sludge in rotary furnaces together with chrome ore and soda, when chromic oxide is transformed into sodium chromate at temperatures around 800oC. This manufacturing method covers almost 70% chromate consumption in the tanning industry. Processing chrome ore together with chrome sludge seems to be a simple solution. However, magnesium oxide has to be removed from the filter cake because it reacts at high temperatures with chromic oxide to produce stable spinel. Magnesium oxide can be removed by leaching the cakes with diluted sulfuric acid, which requires further equipment and has to be managed by processing a diluted magnesium sulfate solution. Ore in rotary furnaces moves against a stream of hot combustion gases and organic substances could pyrolyze in a certain zone to produce tar which could endanger dust filters and electrostatic precipitators. Evidently, a high capacity-furnace operator will not risk its function at the price of processing a comparatively small quantity of chrome waste.

Due to all these complications, we worked on possibilities of oxidizing chrome cake in the liquid phase with oxygen under an increased temperature and pressure. We carried out several preliminary tests in an alkaline medium at a temperature of 160oC and under 1-MPa pressure. Using pure oxygen, a practically 100% oxidation of the organic fraction was achieved,

all the chromium having been converted into an alkali magnesium chromate. The organic fraction content is relatively high and even with a 5% concentration of dry substance in the feed, adiabatic heating is about 200 K. A diagram of the technology we propose is shown in following Fig. 3. However, this presented method of processing filter cake will demand further research which we are at present intensively conducting.

### 3 Simulation Calculation of Timed Course of Temperature

We assume that the diluting of a filtration cake continues according to the following chemical reaction:



The balance of the differential equation is thus given as:

$$\dot{Q} = k \cdot S \cdot (t - t_o) + m \cdot c_p \cdot \frac{dt}{d\tau} \quad (1)$$

- $\dot{Q}$  flow of temp. developed in the reaction [kg.s<sup>-3</sup>.K<sup>-1</sup>]
- $c_p$  specific temperature of drained mix [m<sup>2</sup>.s<sup>-2</sup>.K<sup>-1</sup>]
- $t$  temperature in the reactor [K]
- $t_o$  temperature of the surroundings [K]
- $\tau$  time [s]
- $k$  coefficient permeable temperature [kg.s<sup>-3</sup>.K<sup>-1</sup>]

Because the weight of the mix in the reactor changes to greater dimension in connection with the addition of oxygen, it is necessary to bring up changes to the weight  $m$ .

$$m_r = m_k + m \cdot \tau \quad (2)$$

- $m_l$  weight of mix the reactor [kg]
- $m$  beginning weight of mix in the reactor [kg]
- $m_k$  weight of flow of sulphuric acid [kg.s<sup>-1</sup>]

After reaching:

$$\dot{Q} = k \cdot S \cdot (t - t_o) + (m_k + m \cdot \tau) \cdot c_p \cdot \frac{dt}{d\tau} \quad (3)$$

We can reflect that is the constant. Acid will be added to the reactor by constant flow, the resulting temperature will thus be constant. After integration equation (3)

$$t = t_o + \frac{\dot{m} \cdot \Delta H_r}{23 \cdot M_k \cdot S} - \frac{\dot{m} \cdot \Delta H_r}{23 \cdot M_k \cdot S} + k \cdot S \cdot (t_o - t_p) \cdot \exp\left(-\frac{k \cdot S}{\dot{m} \cdot c_p} \ln\left(1 + \frac{\dot{m} \cdot \tau}{m_k}\right)\right) \quad (4)$$

where

$t_p$  beginning temperature in the reaction mix [K]  
 $M_k$  molar weight of sulphuric acid [kg mol<sup>-1</sup>]

After the reacting mix reaches to the cooling reactor. Heat accumulation is conducted by the permeable walls of the reactor. The equation has thus the shape:

$$k \cdot S \cdot (t - t_o) d\tau = m_c \cdot c_p \cdot dt \quad (5)$$

We reach the integration:

$$\tau = -\frac{m_c \cdot c_p}{k \cdot S} \ln\left(1 + \frac{t_2 - t_o}{t_m - t_o}\right) \quad (6)$$

If after the temperature  $t_2$  passes the final temperature  $t_k$  (i.e. temperature at which wants that the reactor cools it), time necessary to cool at this temperature is reached.

Expression of temperature  $t_2$  as the function of time  $\tau$  from the equation (6):

$$t_2 = t_o + (t_m - t_o) \exp\left(-\frac{k \cdot S}{\dot{m} \cdot c_p} \cdot \tau\right) \quad (7)$$

Equation (7) expresses the temperature flow in the chemical reactor during cooling. As an example the course of temperature in the reactor in heating and cooling periods is shown in fig. 2.

Entry Data are the following:

Weight flow acid 0.2215 [kg/s]  
 Weight of fraction acid 0.6 [l]  
 Temperature of cooling water 25 [°C]

Beginning Temperature of reactor 40 [°C]  
 Temperature after cooling 40 [°C]  
 Useful capacity of reactor V 2,12 [m<sup>3</sup>]

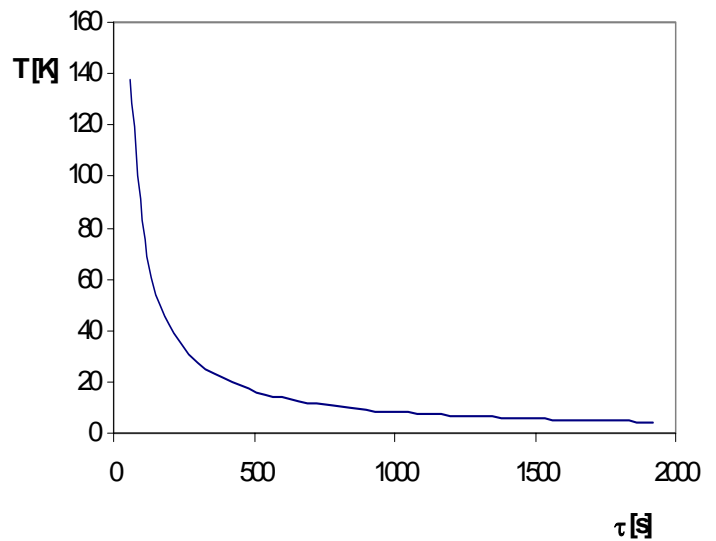


Fig. 2. Course of temperature in the reactor in heating and cooling periods

Cooling surface of reactor S 7,37 [m<sup>2</sup>]  
 Specific temperature capacity  $c_p$  6000 [J/(kg.K)]  
 Coefficient transfer temperature k 200 [kg/(s<sup>3</sup>.K)]  
 Density of cake  $\phi$  1200 [kg/m<sup>3</sup>]  
 Weight of cake in reactor 320 [kg]  
 Density of acid 1374.04 [kg/m<sup>3</sup>]  
 Total weight of sulphuric acid 2541,52 [kg]  
 Maximum temperature 140,029 [°C]  
 Total weight 2861,84 [kg]

A reactor with an inner surface scalded by enamel and a metal mixer were used. Heating was carried out by internal coating 0.6 MPa by sharp steam.

#### 4 Conclusion

We have concentrated on the management of enzymatic hydrolysis of chrome-containing tanning shavings in laboratory and pilot measurements. At the same time we have described the problematics of renewed use of chromate filtration cakes for preparing tanning liquid. Chiefly the methodology of work was mathematical assessment of experimental data with the use of models which correspond to our idea of the given physical-chemical event, i.e. in predominant measure we utilized a heterogenous reaction of kinetics joined with internal diffusion of active components. Next to the determining of these parameters as the

effective diffusion co-efficient of the active compound and the absorption parameters of the appropriate isotherm we used, for the assessment of economic studies, an equation of material and energetic balance of work manifestations of enzymatic dechromation and the processing of chromate cakes.

One of the chief aims of enzymatic dechromation is to acquire a quality hydrolyzate whose quality, among others, is dependent on the contents of remaining chrome. This difficult assignment we successfully completed.

Processing by analytic method and kinetic model made it possible for us to determine minimum main working costs. The conducted economic study thus shows that necessary costs of the product of enzymatic hydrolysis are in the range of 10-15 CZK/kg during the costs of processing.

The chief aim was to conduct working experiments in conditions at a.s. TANEX Hrádek nad Nisou on a working reactor with minimal capacity of 300 kg of reaction mix and to complete the proposal for technology of recycling chrome for the manufacture of tanning chromate salts.

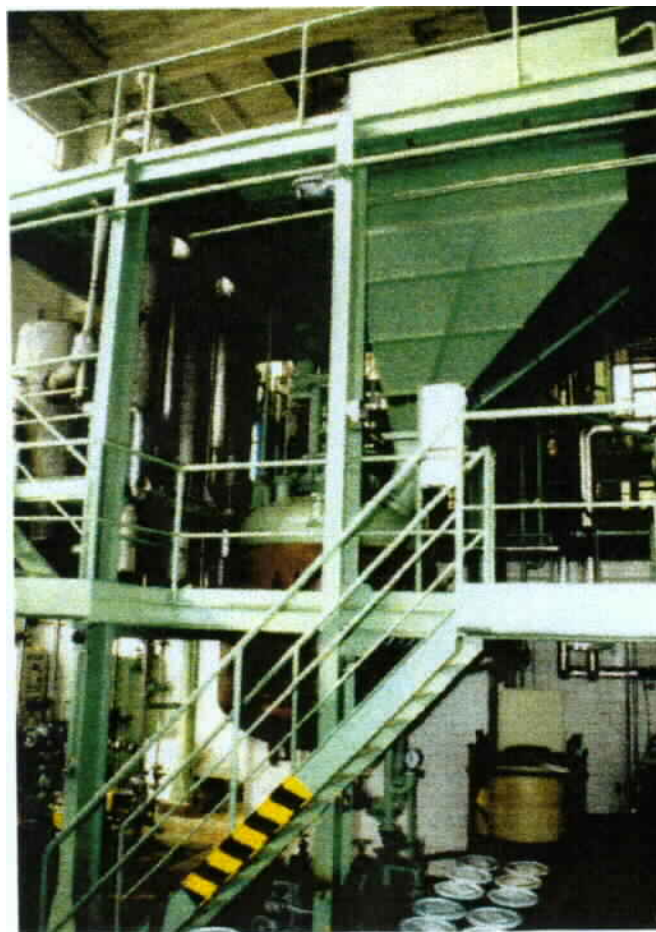


Fig. 3. The Beamhouse TANEX Hrádek nad Nisou

The literary study was aimed at the work of addressing the practical possibilities for liquidating chrome-containing tanning waste. Again it was confirmed that enzymatic processing is currently the most prospective road to resolving this important ecological problem - the liquidation of chrome-containing tanning waste. Considering that already the working results we conducted on a balance of waste, have in the course of the resolution, manifested serious interest of tanning practice in the Czech tanning industry. From this it has been recognized that particularly in recent years, there has been a marked increase in the costs of storing chrome-containing tanning waste, which burdens the manufacturing costs some million parts annually.

Processing filtration chromate cakes in mix with dichromate in the laboratory, experiments and working tests showed very good results. Manufactured regeneration tanning chromate salt provided a leather product whose final quality is quite comparable with those products which were tanned with classically manufactured tanning liquid.

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