Mathematical Model for the Yield of Hydrolysates in Leather Waste Processing

H. Vaskova and K. Kolomaznik

Abstract—Environmental issues increasingly come to the forefront of interests of society, which begins to be aware the current way of using resources of our planet is no longer sustainable. Efforts are being made to use the least environmentally burdening technology which includes those that have solved complex utilization of wastes. Hydrolysis processes offer a reasonable solution for the processing of certain part of wastes produced by leather industry that is besides its useful function perceived as consumer of resources and pollutants producer. Authors of this paper present a mathematical model based on the total mass balance of technology and balance of individual components to optimize the hydrolysate yield. The attention is also paid to the modeling of temperature and determination the time necessary for reaching the ideal temperature for running a hydrolysis process in a reactor. A significant aspect of new technologies is also the economic side. Therefore the mathematical models are associated with the purpose of minimizing of operating costs. Presented technology of tannery waste processing offers safe and environmentally friendly alternative to common ways of waste disposal as landfilling or incineration are, bringing the risk of leakage of hazardous substances into the soil and groundwater or the air.

Keywords**—**Hydrolysis, leather waste processing, mathematical modeling, optimization, tannery waste

I. Introduction

ISSUE of waste reduction and ways of their safe, environmentally and economically favourable disposal is, as a logical result of long-term situation, one of the most actual and pressing global problems. People are surrounded by an occurrence of waste for centuries, but only for decades waste has become a problem that should be systematically solved and organized. The production of various types of waste has an upward trend for decades in a manufacturing sector and even in the public sphere.

A significant amount of waste is produced in the manufacturing sector of natural polymers especially in the leather industry. The leather tanning industry is historically one of the first industries occupying an important function in terms of by-products of other industry - meat industry. However, it is also perceived as a resources consumer and pollutants producer [1]. Tanning industry transforms raw hides of slaughter and game animals through physical and chemical processes to a stable, technically usable product - the leather. On one hand it uses meat industry waste as a feedstock on the other hand this industry produces another hazardous waste.

Production of 200 kg of leather requires one ton of raw hides processing, i.e. feedstock usage is only 20% efficient. From this one ton of raw hides about 250 kg of non-tanned waste, 200 kg of tanned wastes containing chromium is also produced. The remaining share comprises modified solid waste and sludge. In the production of 200 kg of leather about 50,000 kg of waste water containing about 5 kg of chromium is generated.

About 80 – 90 % of the world leather production is chrome-tanned. At the end of the 19th century it was discovered that using complex salts of trivalent chromium in the process of tanning effectively influenced the desired functional properties of leather. Until present time chrome-tanning is the most common and most widely used method. Chrome-tanning brings number of benefits in terms of quality and durability of the product however, the ecological burden and the necessity to deal with the issue of carcinogenic hexavalent chromium. Toxic hexavalent chromium can be formed from mostly beneficial trivalent chromium under a wide range of conditions. Risk of chromium-containing materials lies in the possibility of spontaneous oxidation of trivalent to hexavalent chromium [2] – [4]. Although certain factors to assist the conversion of chromium are known (such as the presence of oxidizing agents, energy in the form of heat or UV radiation, etc.) precise conditions of the spontaneous oxidation has not yet been investigated in detail [5]. Their knowledge is indeed crucial for the safe use of leather products and processing of leather waste. Despite growing demand for alternative methods of tanning, none have been found competitive substitute for a large extend.

In recent years the mathematical modeling gains a great importance for the analysis and prediction of the behaviour of processes and phenomena in areas of natural, technical, industrial, but also economic and social. It offers the possibility to transfer the problem from the field of application to be processed mathematically. This allows to penetrate through the analysis into its nature and to obtain useful information about investigated problem. Using mathematical means and information technology procedures can be created. Procedures, that leads to a deeper and more thorough understanding and influencing real processes and phenomena.

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II. Scope of the Research

Recently, worldwide efforts are being made to implement the automation of processes in the leather processing to increase productivity, accuracy, operation, time efficiency and also facilitate physically demanding work and restrict acts that threaten the health of employees. The literature search shows that the automatic control of hides, respectively tannery waste processing is not very widespread and the level of using diagnostic and automated systems is quite low. Rather, automated and robotic equipment in the secondary manufacturing are used than automatic control of processes. Problematic for the application of measurement and control systems in the leather industry is obtaining information on the technological process due to aggressive and non-homogeneous environment and also the lack of quantitative models allowing the use of some modern management methods. An integral part of the automated control implementation is mathematical description of the basic processes and mathematic modeling. This is our effort – to increase this level and to prepare the way for better, optimized design or control of the modeled processes.

III. Theory

A. Waste of leather industry

Leather products like shoes, belts, wallets, upholstery and others belong among the objects of everyday needs. Achieving the final products comprise a lot of waste arising from the raw material processing (tannery waste) and manufacturing specific items (manipulation waste). These are two types of leather waste. Another arises when these mentioned objects become unusable and are moved mostly to landfill or incinerators. This third waste category of old "retired" leather stuff may represent a serious threat to the environment.

The majority of global leather production is chrome-tanned. Using complex salts of trivalent chromium in the process of tanning effectively influenced the desired functional properties of leather. Trivalent chromium stabilizes a hide by crosslinking the collagen fibres and supply required qualities. However, trivalent chromium contained in leather can be under various conditions in small amounts oxidized to another form – hexavalent chromium.

Hexavalent chromium (CrVI) unlike trivalent chromium (CrIII) is toxic and carcinogenic element. A potential threat to the health could be hidden in chrome-tanned leader goods, mainly shoes, which are in daily contact with the human organism. If the goods contain even small amounts of carcinogenic chromium, there is a potential risk of cancer, especially kidney and urinary tract [3]. The effects of repeated exposure to hexavalent chromium have hazardous impact on human health [6, 7].

The possibility of the spontaneous oxidation of CrIII into CrVI can occur both in alkaline and acidic medium in the wide range of pH what complicate the right conditions specification [3]. Trivalent chromium contained in discarded leather items may succumb to uncontrolled oxidation on the landfills and make the waste hazardous, which may result in the possibility of leakage into the soil and groundwater.

B. The dechromation process of leather waste

Hydrolysis, as a decomposition reaction is significantly used in technological processes for the purpose of fermentation of the matrices (e.g. leather wastes) for subsequent analysis of the studied material. Hydrolysis of collagen material in alkaline or acidic medium is used also in a complex process dechromation of the leather industry wastes. In these cases, one component - chromium or protein is subjected to liquefaction. Therefore this substance can be also utilized effectively into other forms.

The structure of the entire dechromation process of tannery wastes e.g. chromium shavings, is displayed in Fig. 1.

The first stage - the process of dechromation of chrome-tanned waste i.e. a separation of liquefied collagen protein from chromium sludge was already resolved in our institute and the technology for this process was realized in laboratory conditions. In [8, 9] a whole computer system for chromium recycling with focus on the control structure of the most important parts of the technology is described. Obtained chromium sludge can be subsequently revitalized and acquired chromium in a form of salts can be used for further leather tanning [10]. High-quality gelatinous protein can be obtained in this stage. It finds applications in food industry, pharmaceutical industry or cosmetics.

The second stage is enzymatic hydrolysis. Undecomposed protein is hydrolysed under the act of proteolytic enzymes that facilitate the cleavage of bonds in molecules. The molar mass

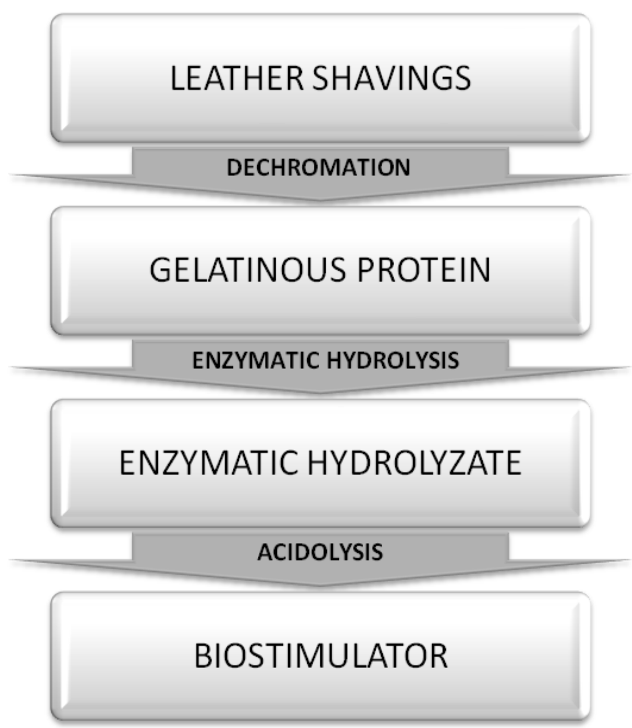


Fig. 1 Structure of collagen protein hydrolysis process

Fig. 3 Diagram of the production system for two-stage process

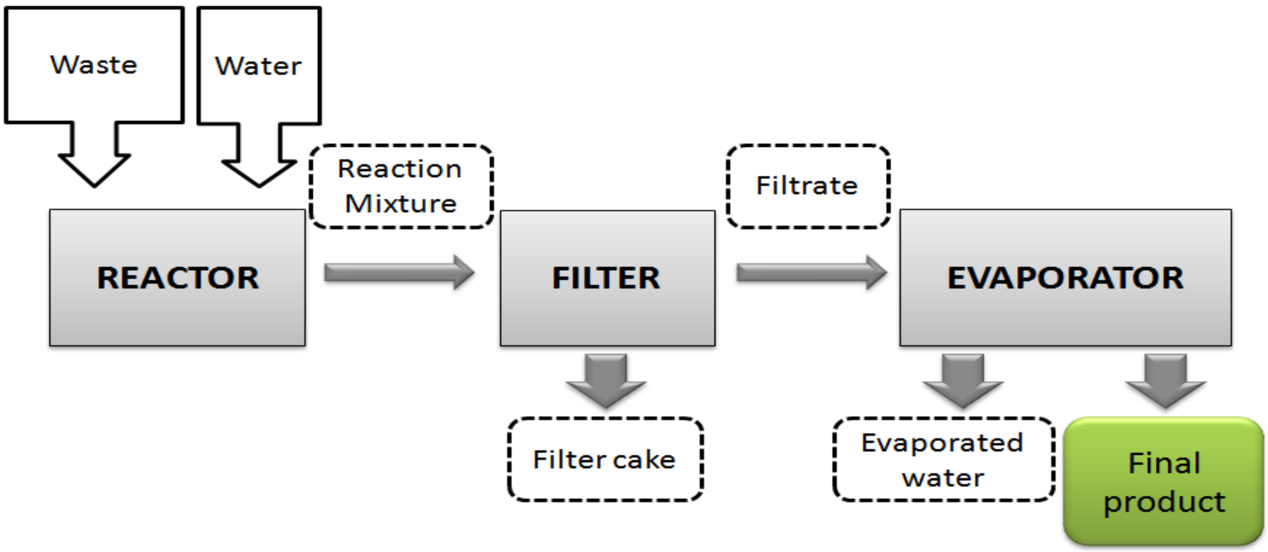
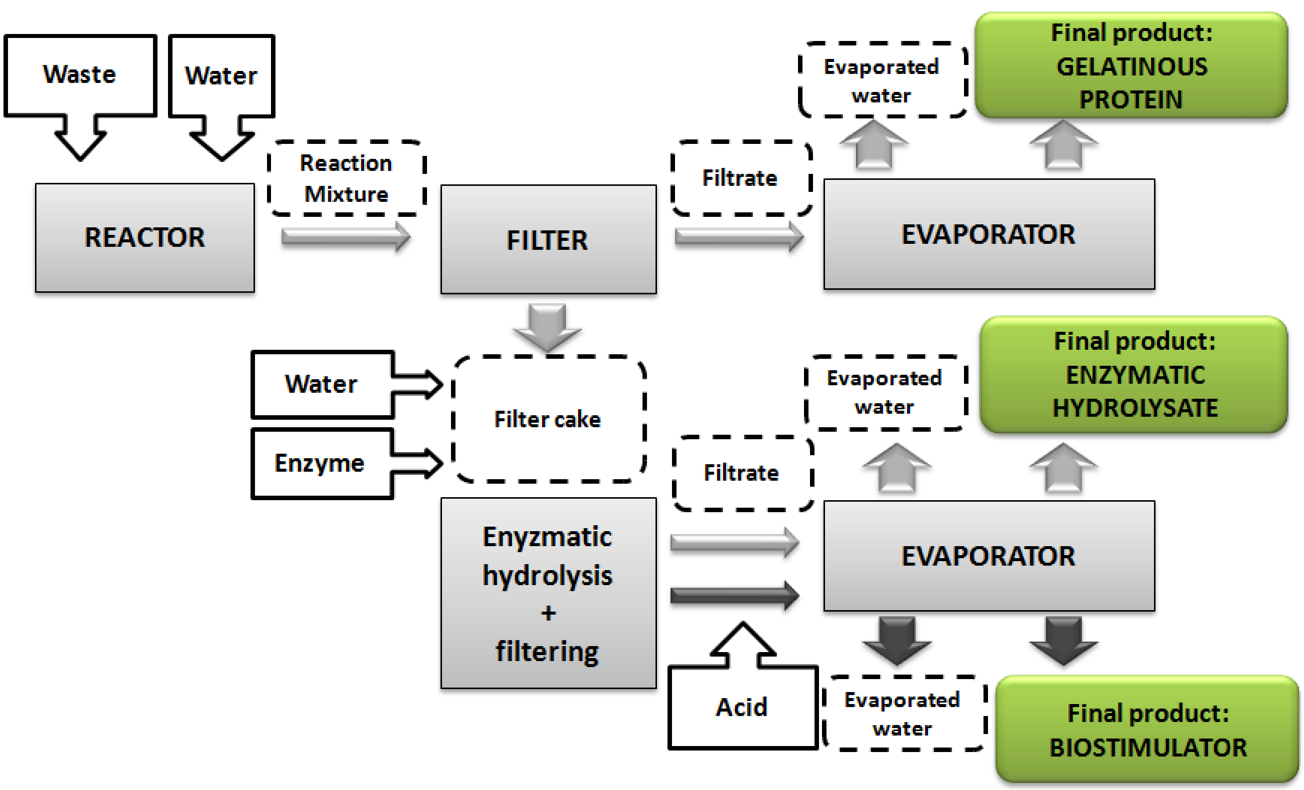


Fig. 2 Diagram of the production system

is lowered and an enzymatic hydrolysate is obtained. To eliminate the share of waste material there exist an option for hydrolyzates usage in agriculture such as inducers of resistance or biostimulator [11]. For this application it is necessary to achieve even stronger molar mass reduction. A plant is then able to absorb the hydrolyzate and run the immune mechanism as a protection against diseases. This molar mass decreasing is possible to achieve by acid hydrolysis.

C. Production system

The production system for producing of the hydrolysate is composed of three basic elements: the reactor, the filter and the vacuum evaporator. The simplified diagram is shown in Fig. 2. Feedstocks in the reactor are leather waste, water and an alkali, creating a reaction mixture. When the desired degree of hydrolysis is reached, hot heterogeneous mixture is filtered and the resulting filtrate is further transferred to an evaporator, where the concentration of hydrolysed substance is increased.



In the case of two-stage process, shown in Fig 3, the technology continues to enzymatic hydrolysis of a filter cake which is transferred to a reactor, pH is checked, adjusted if necessary . The mixture is heated to the desired temperature of

Table 1 Physical quantities and their assignments for model formulation

Designation	Physical quantity	Unit
CH	Mass of leather shavings	t
W	Mass of water (the feedstock)	t
FK	Mass of filter cake	t
P	Mass of product	t
WO	Mass of water (waste material)	t
FL	Mass of filtrate	t
$a_{s,CH}$	Amount of dry matter in leather shavings	1
$a_{s,FL}$	Amount of dry matter in filtrate	1
$a_{s,P}$	Amount of dry matter in product	1
$a_{s,FK}$	Amount of dry matter in filter	1

70 ° C and a proteolytic enzyme added. Another procedure is the same as in the first instance. If we want to further reduce the molar mass (particularly for agricultural applications), it is necessary to undergo acid hydrolysis, using e.g. phosphoric acid or nitric acid.

The list of physical quantities fundamental for the description and setting the mathematical-physical model are

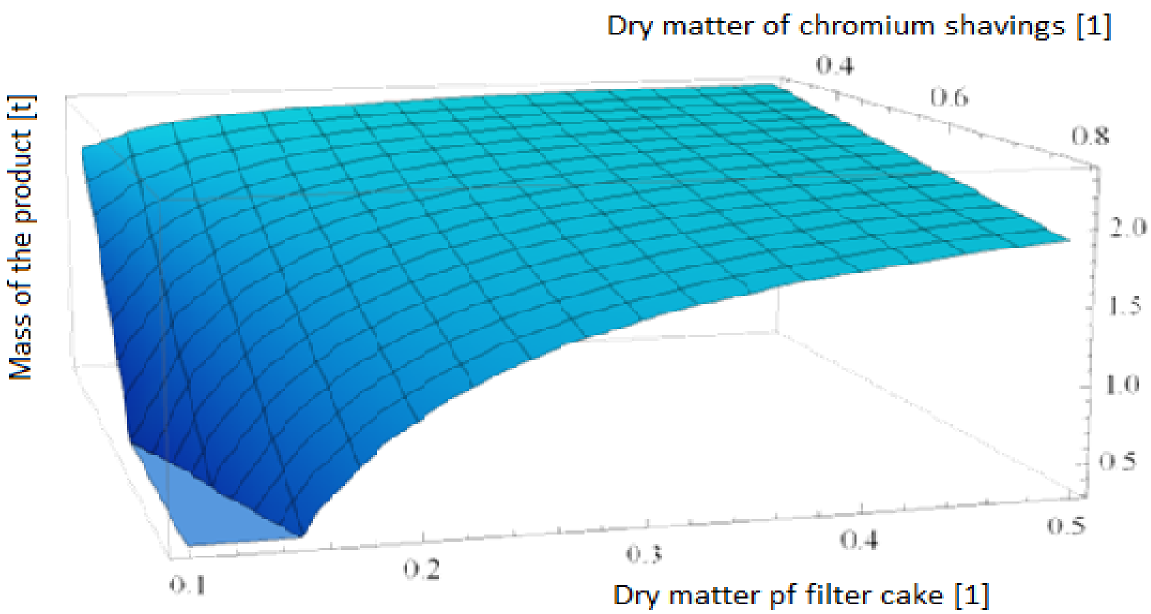
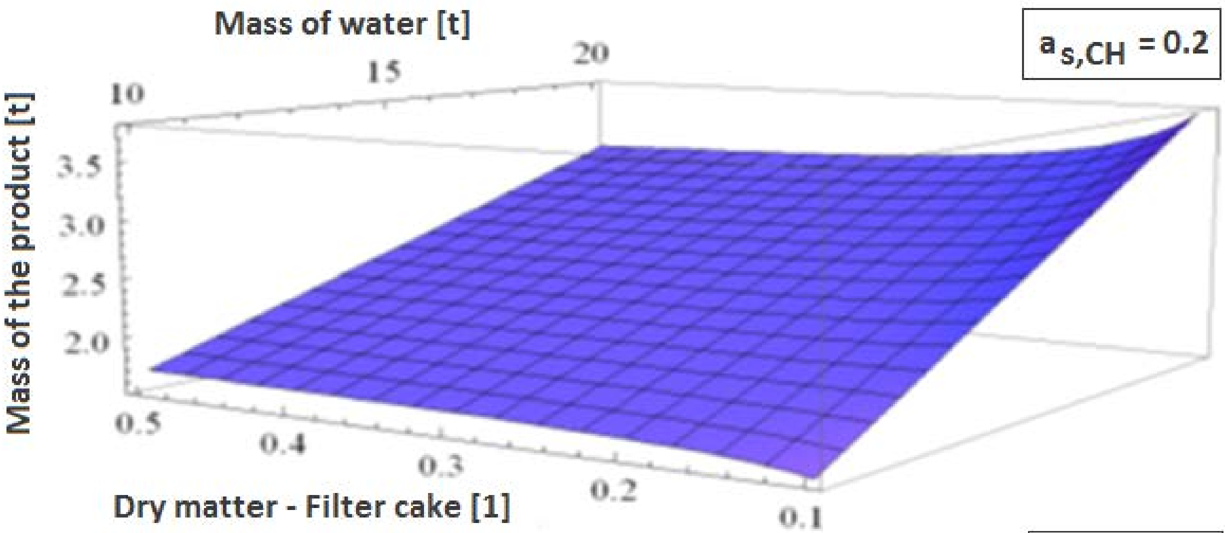
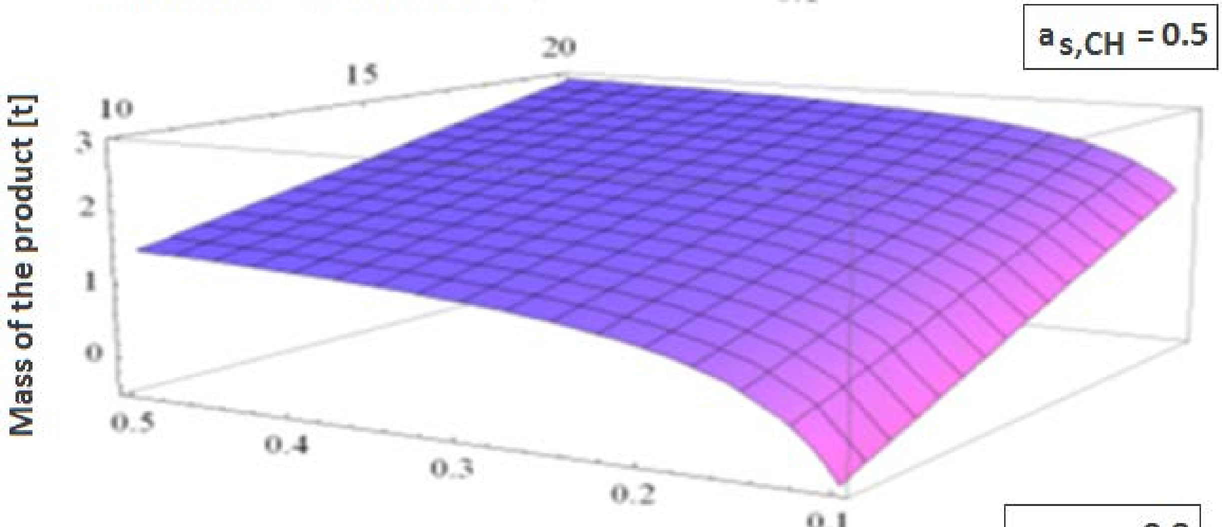
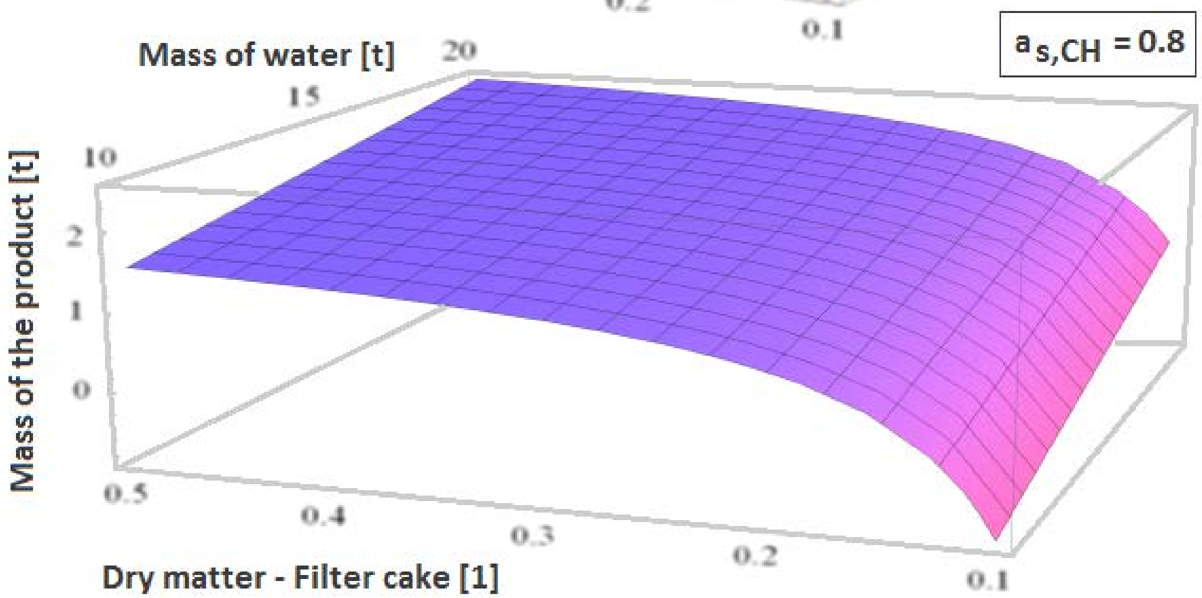


Fig. 4 3D mathematical models for hydrolysate yield optimizing: dependence of the mass of product on the dry matter of chromium shavings and on the dry matter of filter cake.


Mass of water [t]
20
15
10
Mass of the product [t]
3.5
3.0
2.5
2.0
0.5
0.4
0.3
0.2
0.1
Dry matter - Filter cake [1]
$a_{s,CH}$ = 0.2


20
15
10
Mass of the product [t]
3
2
1
0
0.5
0.4
0.3
0.2
0.1
$a_{s,CH}$ = 0.5


Mass of water [t]
20
15
10
Mass of the product [t]
2
1
0
0.5
0.4
0.3
0.2
0.1
Dry matter - Filter cake [1]
$a_{s,CH}$ = 0.8

Here FK, P, WO and FL are unknown quantities. The objective is to gain as much product as it is economically profitable with the consideration of the main operating costs. The objective function consists out of costs of filtration and drying costs.

Simulation calculation was performed for known values of dry matter of individual compounds listed in Table 2. The amount of feedstock was chosen for a real reactor in semi-industrial scale - 3 tons of leather waste and 15 tons of water. The mass rate of leather shavings and water is already known from foregoing experiments and laboratory experience.

Table 2 Values of dry matters

Physical quantity	Value
$a_{s,\,CH}$	0,2 – 0,8
$a_{s,\,FL}$	0,04
$a_{s,\,P}$	0,3
$a_{s,\,FK}$	0,1 – 0,5

B. Results

Wolfram Mathematica software was used for visualization of the solution of mass balance mathematical models. 3D model in Fig 4 represent the dependence of product mass on the dry matter of chromium shavings and the dry matter of filter cake or water consumption.

It is also necessary to consider varying value of dry matter of

feedstock material due to various sources of leather waste what will also affect the quality of filtrate. Dry matter of FK depends on the time of filtration and on pressure energy consumption.

Considering the objective function, it is clear from Fig. 4, that from approximately 30% of dry matter of FK it does not have a significant effect on the yield of the product to continue with filtration. Continuing to the process would extend the time and consumption of energy thereby the costs.

In Fig. 5 3D dependences of hydrolysate yields on the dry matter of filter cake and the consumption of water for a specific mass of dry matter of chromium shavings are displayed. These results show how the product yields develop in a range of dry masses of chromium shavings. The most remarkable change occurs for lower amounts of dry matter of filter cake. Also the consumption of water for reaching the same product yield increase with the higher amount of dry matter in leather shavings.

Fig. 6 presents the dependence of the product yield on the try matter of chromium shavings and the consumption of water for the 30% of dry matter in filter cake.

V. Temperature modeling

For the purpose of costs optimization it is necessary to determine the time needful to achieve the optimal temperature for the running of hydrolysis reaction. Mathematical-physical

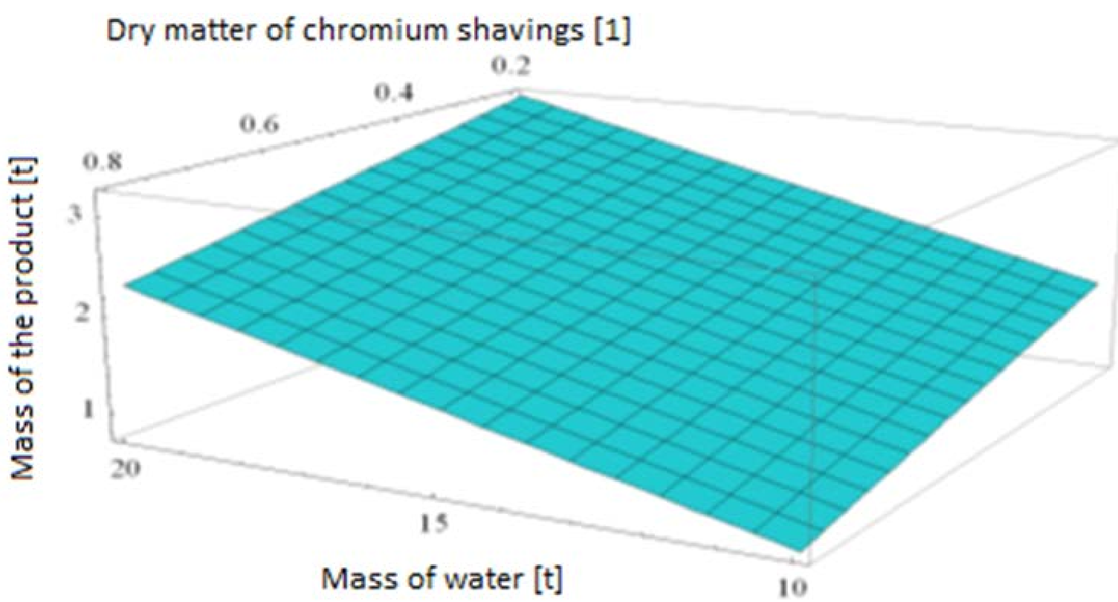


Fig. 6 Dependence of the mass of product on the dry matter of chromium shavings and the consumption of water for value 0.3 for the dry matter filter cake

model is based on the balance of heat outputs in a flow reactor (in terms of heating). The main part of the reactor has a cylindrical shape. Its lower part forms a cone and the upper part has the shape of a spherical cap. Cylindrical and the lower part is heated by heat transfer medium – a steam and is

isolated from the surroundings, what does not apply to the spherical cap. The scheme of the reactor is displayed in Fig. 7. The main parameters of the reactor and other important physical quantities are listed in Table 3.

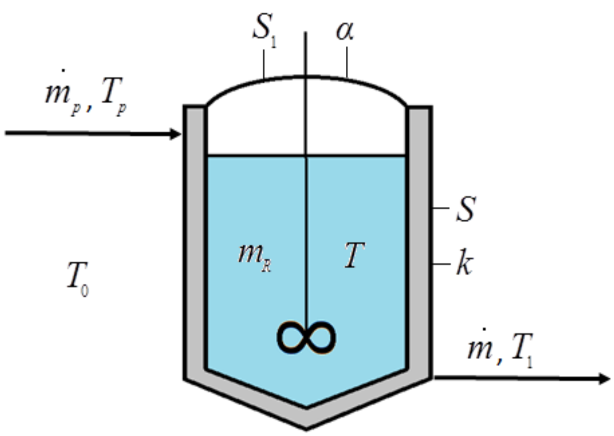


Fig. 7 Chart of the reactor

Table 3 Physical quantities and assignments for the model (5)

Symbol	Physical quantity	Unit
τ	Time	s
T_0	Ambient temperature	°C
T	Temperature of the reaction mixture	°C
T_1	Temperature of the condensate	°C
T_p	Temperature of the heating steam	°C
c_p	Specific heat of water	$J kg^{-1}K^{-1}$
k	Heat transfer coefficient	$Wm^{-2}K^{-1}$
α	Heat transfer coefficient of the reactor lid	$Wm^{-2}K^{-1}$
H	Heat of condensation of steam	Jkg^{-1}
$\dot{m}_p$	Mass flow of heating steam	kgs^{-1}
r	Radius of the reactor cylindrical part	m
h	Height of the reactor cylindrical part	m
v_1	Height of a spherical cap	m
v_2	Height of the conical part of the reactor	m
S	Area of the reactor heated by steam	m^2
S_1	Surfaces of the reactor (spherical cap)	m^2

A. Temperature model

The balance of the heat outputs is given by the differential equation

$$H\dot{m}_p + \dot{m}_p c_p (T_p - T_1) = \\ = kS(T - T_0) + \alpha S_1 (T - T_0) + m_R c_p \frac{dT}{d\tau} \quad (5)$$

Considering the initial conditions

$$\tau = 0, T = T_0 \quad (6)$$

The solution is:

$$T = T_0 + \frac{A}{B}(1 - e^{-\frac{B}{D}\tau}) \quad (7)$$

Where A, B and D are constants introduced to simplify the model solution

$$A = H\dot{m}_p + \dot{m}_p c_p (T_p - T_1) \quad (8)$$

$$B = (kS + \alpha S_1) \quad (9)$$

$$D = m_R c_p \qquad (10)$$

Graphs based on temperature model (5) i.e. model of the influence of the initial temperature for the achievement of the reaction temperature are presented in Fig. 8 and Fig. 9. Results show there is a difference in time about 15 minutes for the ambient temperature in the range 5°C – 30 °C.

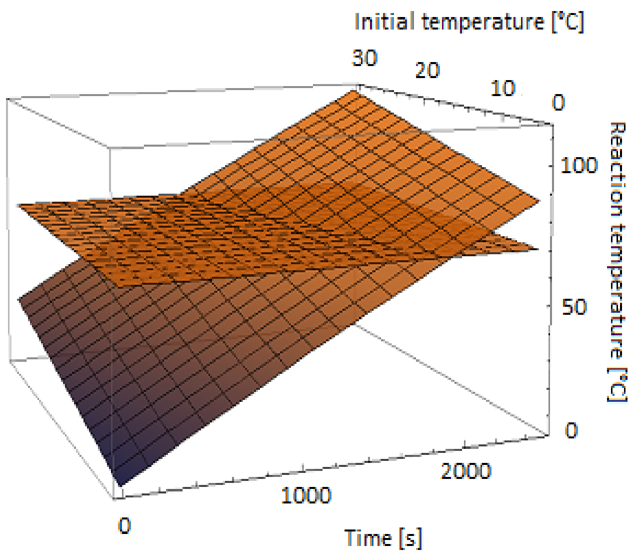


Fig. 8 Dependence of achievement the reaction temperature on the reaction mixture initial temperature.

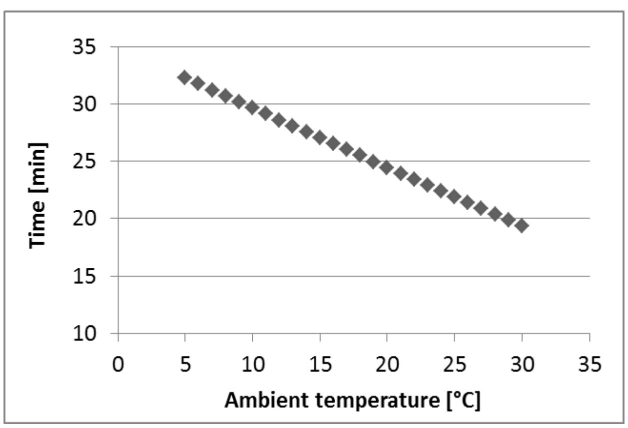


Fig. 9 Time interval for the desired temperature of hydrolysis reaction achievement

VI. Conclusion

The method of safe and environmentally friendly way of leather waste reduction based on hydrolytic processing of collagen material is solved. This issue is within one of the actual global problems. Models and simulation studies dealing with the requirement of optimal hydrolysate yield in the process of leather waste reduction and time and thermal efficiency were presented. Mathematical models are related also to the economic aspects of the process leading to optimization of operating costs. The optimization of manufacturing processes of leather wastes is based on thorough analysis of technological operations and on design of mathematical models describing the mechanism of their behavior.

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Karel Kolomaznik was born in Kromeriz, Czech Republic. He took up an academic position in Zlín in 1970 at the Faculty of Technology of Brno University of Technology (which was later changed to Faculty of Technology of Tomas Bata University in Zlín). Since 2006 he has been working at the newly established Faculty of Applied Informatics. His research group deals with optimization of technological processes particularly in the field of processing waste generated by tanning, leather and food processing industries into valuable products.

He has led and participated in many successful projects funded e.g. by the Ministry of Education, Youth and Sports of the Czech Republic, Ministry of Industry and Trade or the Ministry of Agriculture, the Czech Science Foundation, the US-Asia Environmental Partnership program, etc. In addition to that, he has put most of his results into industrial practice in cooperation with commercial partners from both the Czech Republic and abroad. He has had a long-term cooperation with the Eastern Regional Research Center of the U.S. Department of Agriculture, Wyndmoor, PA where he successfully applied the ammonia-free deliming of white hide. In the NIKE Inc. (Ho Chi Minh City, Vietnam) he implemented a patented technology for the processing of manipulation waste from leather industry including the application of the products. He has been also active in industrial applications within the Czech Republic, e.g. implementation of a patented technology of a protein hydrolyzate production from animal-based organic waste in the Kortan, s.r.o. in Hrádek nad Nisou.

Prof. Kolomaznik was awarded in 1998 the “Rolex Award for Enterprise”, for the technology of processing and recycling of potentially hazardous chrome-tanned waste produced by the leather industry. In 2009 he received the ALSOP Award of the American Leather Chemists Association for his long-term contribution to the association and the leather industry.