Additives and Advanced Biomaterials Obtained from Leather Industry by-products

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Animal skin/hide as the by-product of the meat processing is reclaimed by the leather manufacturing industry which generates large amounts of hide and leather wastes containing proteins, fatty matters, sodium, calcium, chromium and other inorganic salts. Processing such wastes is impaired by their high water content, difficulties in the protein separation from fatty matters or deleterious chromium compounds. This paper presents some innovative processes for reclaiming the proteins carried by a large variety of leather wastes, along with the fatty matter separation and transesterification to obtain biofuels for heating plants. Several other products, as biofertilizers and surfactants intended to be used in the concrete manufacture have been obtained from the hide waste protein hydrolysates.

Keywords: bioactive collagen hydrolysate, protein by-products, biofuel, biodiesel, foliar fertilizer, surfactants

In the last years, several advanced technologies were introduced in the leather wastes handling and treatment for chemical stabilization and valuable products recovery. Mainly, they have been focusing on the proteins [1-5], fatty matters [6, 7] and chromium compounds [8] separation, which by further chemical treatments were converted to useful commercial products.

This paper presents some of the new ways for hide waste and leather waste reclamation through chemical hydrolysis, solvent extraction, methanolysis or other processes bound to the conversion of this raw waste into collagen hydrolysates and amino-acids ready to be used in foliar fertilizers formulations, biofuels for heating plants, as well as surfactants for light concrete manufacture. Approach of this subject included a multistep process with defined purpose to remove all deleterious matter from both hide and leather waste and to recover the protein and fats as raw materials, which can be converted into add-value products through protein hydrolysis and fat methanolysis. Different processing patterns were developed, starting with proteins alkaline hydrolysis and conversion into collagen hydrolysate without chromium up to fats extraction and methanolysis for their conversion into heating biofuels. Further development concerns the use of collagen hydrolysates containing amino-acids as components of biofertilizers following some other innovative pathways than those found in literature [9].

Experimental part

Materials

a) Leather wastes from SC Pielorex SA tannery with the following composition: 54.1 % water, 9.9 % ash, 4.7 % Cr₂O₃, 15.0 % total nitrogen, 84.3 % hide substance (% based on dry matter), and pH = 3.5; b) Bovine hide wastes from SC Pielorex SA tannery, with the following composition: 79.2 – 82.6 % water, 20.5 – 26.1 % ash, 19.0 – 32.0 % fats, 9.0 – 12.2 % free fatty acids, 7.8 – 10.62 % total nitrogen, 7.5 – 10.3 % protein nitrogen, 41.9 – 58.1 % hide substance, 7.9 – 8.6 % CaO, 0.92 – 1.15 % Na₂S, 11.7 – 16.2 % NaCl (% based on dry matter), and pH = 11.8 – 12.5; c) Chemicals: CaO technical product, over basic potassium naphthenate purified, granulated urea, ethanolamines p.a., H₃BO₃ p.a., Zn(NO₃)₂ p.a., Cu(NO₃)₂ p.a., Mn(NO₃)₂ p.a., methanol p.a., potassium hydroxide p.a., sodium hydroxide p.a., sulphuric acid p.a., n-heptane, biodiesel (based on methyl esters of sunflower fatty acids, prepared by the authors).

Methods

Collagen hydrolysate was obtained from the alkaline hydrolysis of chrome leather wastes under the reaction conditions optimized by mathematical simulation of alkaline hydrolysis at atmospheric pressure leading to protein hydrolysates of 7000-12000 Da molecular weight. The optimized process was carried out in a batch reactor provided with a vapor condenser and automatic temperature control at a temperature of 79.5-80.0°C for 6.5 h; Characterization of collagen hydrolysates was performed by classical analyses (solid, total ash, total nitrogen contents, and pH). Sorensen method [17] and polycrylamide gel electrophoresis (SDS-PAGE technique) was used for molecular weight measurements, the atomic absorption spectrometry (AAS, Thermo Instruments) for the residual chromium determination and the HPLC (Thermo Electron – Finningen Surveier) with DAD detector (Diode Array Detector) for the qualitative and quantitative determination of amino-acids.

Preparation of foliar biofertilizers with protein additives for plant growth was based on previously tested foliar fertilizer formulas [10-13] containing macro-nutrients, micro-nutrients and stabilizers able to graft with protein additives such as collagen hydrolysates with no losing out on their adequate properties required for foliar application. Trial runs with the new foliar biofertilizers were carried out to assess their growth stimulating action on vegetable crops.

Obtaining the biofuels for heating plants and biodiesel. Untanned hide waste was treated in acid medium at a temperature of 95°C for hydrogen sulphide removal and neutralization. After this preliminary treatment, fatty matters were separated by extraction with n-heptane and were characterized by the following specific parameters: saponification index = 196.7 mg KOH/g, acidity index = 5.2 mg KOH/g, iodine index = 52.3 g I/100 g and water

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content = 0.05 %. Fatty matters recovered after the n-heptane removal were treated at 60° under heavy stirring with a solution of potassium methoxide (methanol: fatty matter molar ratio of 5:4:1 and KOH: fatty matter mass ratio 1/99). Further, fatty acid methyl esters (FAME) were separated from the raw glycerin and refined by successive water washings. Final steps in the purification of FAME were the volatile compounds removal by heating under vacuum and treatment with whitening earths. Thus, a biofuel containing 96.8 % methyl esters with the pour point 10°C was obtained. Also, the above procedure was improved by replacing the n-heptane with biodiesel obtained by methanolation of sunflower oil (biodiesel: fatty matter 1:1 and 2:1 molar ratios based on the original fatty matter weight percentage in raw material). Fatty matters dissolved in biodiesel were subjected to methanolation under milder conditions than those referred above, namely under strong stirring at the room temperature for 45 min. The reaction product was a biofuel containing 97.1% methyl esters with the pour point 4°C (fatty matter molar ratio 1:1) and respectively a 97.5% methyl esters biofuel with the pour point 0°C (biodiesel: fatty matter molar ratio 2:1). Other details of the procedure are described in our previous papers [14, 15].

Gas-chromatography analysis of biofuels. The GC was used to find the fatty acid composition of biofuels. Samples (1 μL) were injected into a PerkinElmer 500 Clarus gas-chromatograph equipped with a SGE BX 70 capillary 50 m in length column, film thickness of 0.25 μm and ID of 0.22 mm. In all experiments the splitting ratio in the splitting injector was 50:1 and the flame ionization detector (FID) was fed at a rate of 40 mL/min carrying gas.

Obtaining the additives based on the protein hydrolysates and alkaline soaps for the concrete manufacture. Untanned hide wastes with low fatty matters content, which cannot be processed by the fat extraction and transesterification, were subjected to the alkaline hydrolysis in a digester equipped with a stirring system at 150°C for 12 h. The resulting mixture was cooled down to 20°C and the insoluble residues were separated by filtration. Filtrate containing 19.05 % solids (measured by DSC), including protein hydrolysates and alkaline soaps, was showing surfactant and foaming characteristics, which enable their use as air pore former additive, in light concrete manufacture [16].

Results and discussions
Optimizing the chrome leather waste hydrolysis
Mathematical simulation of the alkaline hydrolysis process was foreseen as mean for setting up best working parameters of this stage carried out under atmospheric conditions. The optimization target of the simulation is to achieve a minimum molecular weight of the collagen hydrolysate (y). Many factors can influence the hydrolysis process, but from preliminary investigations correlated with literature data [3] two process parameters aroused as significant variables (n=2): temperature (z1) and reaction time (z2) [17].

Entire research was organized according to some factorial programs applied in three stages. First stage concern full factorial experiment on the basis of EFC 2ⁿ program, which results in an auxiliary mathematical model expressed as a linear equation providing information about the further experiment development direction. In the second step, modeling advancement is made toward the optimum zone using Box-Wilson method. The advancement is progressing as far as the experimental data are in good agreement with the predicted data by the linearly equation derived in the first step. The point where computed data are marked clearly of inconsistency against experimental data in the center of a new modeling step resulted in an auxiliary mathematical model, substantiated through a polynomial with two variables, n = 2. This equation was used for optimal parameters computation, which when introduced in the mathematical model allow the identification of two optimal operational parameters area of the hydrolysis process parameters.

The point of z1 = 70°C and z2 = 4 h coordinates was chosen as the experiment center, and the variables Δz1 = 20°C and Δz2 = 2 h were selected as parameter variation intervals. Under these circumstances, the settled experimental conditions were as follows z1 = 90°C , z1 = 50°C, z2 = 6h, z2 = 2h. Because neither auxiliary mathematical model nor final mathematical model is operating with natural variable z1 and z2 there were introduced the "encoded" variables which take only the values ± 1: xi = zi ± 2 (i = 1, 2). The experimental results are presented in table 1.

<table>
<thead>
<tr>
<th>Points</th>
<th>x0</th>
<th>Process variables</th>
<th>Process performance (molecular weight), y</th>
<th>Variance s²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x1</td>
<td>z1</td>
<td>x2</td>
<td>z2</td>
</tr>
<tr>
<td>1</td>
<td>+1</td>
<td>-1</td>
<td>50</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>+1</td>
<td>90</td>
<td>-1</td>
</tr>
<tr>
<td>3</td>
<td>+1</td>
<td>-1</td>
<td>50</td>
<td>+1</td>
</tr>
<tr>
<td>4</td>
<td>+1</td>
<td>+1</td>
<td>90</td>
<td>+1</td>
</tr>
</tbody>
</table>

* determined by Sörensen method

- Table 1
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The mathematical model coefficients were calculated from the expression:

\[ b_i = \frac{1}{4} \sum_{j=1}^{3} x_j y_j, \quad i = 1, 2, \]

and the resulting linear model may be written as:

\[ \hat{y} = 19312.5 - 2937.5x_1 - 2862.5x_2. \]

For demonstrating if the model is in good agreement or not with the experimental data, a statistical analysis was carried through, according to the following stages: calculating the variance in all experimental points, checking their homogeneity by Gauss criterion, determining the experimental error (reproducibility variance) and agreement variance as a measure for the error introduced by the model, and model concordance test with the Fisher criterion. It was found in the investigated range that the relation \( \hat{y} = f(x_1, x_2) \) is linear and the model is adequate (\( F_c < F_T \)), because it is easy to see the mean experimental values are very close to those calculated in four experimental points:

<table>
<thead>
<tr>
<th>Experimental values</th>
<th>25100</th>
<th>19250</th>
<th>19400</th>
<th>13500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated values</td>
<td>25112</td>
<td>19238</td>
<td>19387</td>
<td>13513</td>
</tr>
</tbody>
</table>

Such a model, acting as a “compass”, was used in the further investigations to come close to the optimal value searched for. In the next investigation stage it was carried out an experiment inside the area of the optimum values searched for, using the gradient method for this purpose, namely the Box-Wilson method. Under such conditions, the resulting regression equation is:

\[ \hat{y} = 19312.5 - 2937.5x_1 - 2862.5x_2 \quad (1) \]

and describes the process adequately as was revealed by the previous experiments.

Because the statistic analysis has shown that the above model is adequate and the area described by it is planar and, therefore, far from the optimum value searched for, the local optimum had to be found by successive addition of the gradient constituents at the factor zero level. Resulting factor values were introduced in the encoded regression equation (\( x_j \)) to obtain the calculated values for the process performance (\( \hat{y} \)). Five steps were run over and the calculation results were compared to the mean experimental values (table 2).

When the calculated values (\( \hat{y} \)) were compared with the mean experimental value (\( \bar{y}_{exp} \)), only up to the second step an agreement there was revealed a fair agreement. Therefore, the point of \( z_1 = 80^\circ \text{C} \) and \( z_2 = 5 \) hours coordinates has to be considered the centre of a new experiment. This time the experiments based on a quadratic program PO2 (quadratic orthogonal program). This program contains \( N = N_c + N_\alpha + N_0 \) experimental points, where \( N \) - represents the total points in PO2 program; \( N_c \) - the number of experiments in a program \( EFC 2^n \) \( (N_c = 2n) \); \( N_\alpha \) - so called “star points” \( (N_\alpha = 2n) \); \( N_0 \) = the number of repeated determinations in the center of program \( (N_0 = 1) \). The following steps were run over in developing the PO2 program:

- based on the previous step results, there were chosen: a) the point of \( z_1 = 80^\circ \text{C} \) and \( z_2 = 5 \) hours coordinates has to be considered the center of experiment and b) the variation interval values \( \Delta z_1 = 10^\circ \text{C} \) and \( \Delta z_2 = 1 \) h
- these initial data were used to compute the factor values in the four points of EFC 2 program, which are involved in the PO2 program, according to the following equations:

\[ z_1^{(-1)} = z_1^0 - \Delta z_1; \quad z_1^{(+1)} = z_1^0 + \Delta z_1. \quad (2) \]

- the coordinates of the four “star points” \( (z_1^{(\pm \alpha}), z_2^{(\pm \alpha)}) \) were searched by means of \( \alpha \) (“star arm”) variable, whose value was obtained from the biquadratic equation below:

\[ \alpha^4 + 2\alpha^2 \cdot \Delta \gamma - 2\gamma^2 (\alpha + 0.5N_\alpha) = 0 \quad (3) \]

The effective solutions for the equation (3) that could be considered have been \( \alpha = \pm 1 \):

\[ z_1^{(-\alpha)} = z_1^0 - \alpha \cdot \Delta z_1; \quad z_1^{(+\alpha)} = z_1^0 + \alpha \cdot \Delta z_1. \quad (4) \]

Accordingly, the PO2 program obtained from the above data is presented in the table 3.
The complete matrix of the PO2 program requires the calculation of the regression equation coefficients which are presented in the table 4.

The mathematical model represented by a quadratic regression equation with two variables is:

\[ y = b_0 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + b_5x_2^2 \]

Equation (6) was subjected to a statistical analysis to find out if the above model is adequate or not. The reproducibility variance, agreement variance and Fisher criterion value were calculated. As the calculated value \((F_c)\) for the Fisher criterion is less than its tabled value the equation (6) representing the mathematical model is certainly describing the investigated process and ready to be used for further optimization.

As the methodology used to find out optimum regime of the process is dependent on the answering surface (elliptical or hyperbolical paraboloid), the mathematical model represented by the regression equation (6) was brought first to a canonical shape, resulting the relation:

\[ \hat{y} = 20056 + 850x_1 - 2700x_2 - 125x_1x_2 + 1316.7(x_1^2 - a) - 3533.3(x_2^2 - a) \]  

and respectively:

\[ \hat{y} = 20056 + 850x_1 - 2700x_2 - 125x_1x_2 + 1316.7x_1^2 - 3533.3x_2^2 \]  

Because the canonic coefficients have shown opposite signs \((1317.5\) and \(-3534.1)\), the answer surface is a hyperbolic paraboloid, and in this case Lagrange multiplier method is commonly used to finding out the optimum process parameters.

The following equations system was developed:

\[ \begin{align*}
(b_1 - \lambda)x_1 + 0.5b_1x_1 + 0.5b_2 = 0 \\
0.5b_2x_1 + (b_2 - \lambda)x_2 + 0.5b_2 = 0
\end{align*} \]

where \(\lambda\) is the Lagrange multiplier. This system was solved for various \(\lambda\) values so that the process performance \((y)\) to meet the condition: \(y < 10000\). The following results were obtained:

I. For \(\hat{y} = 10000\), \(\hat{x}_1 = 0.058\); \(\hat{x}_2 = 1.345\;\lambda = -4534.6\).

II. For \(\hat{y} = 9000\), \(\hat{x}_1 = 0.058\); \(\hat{x}_2 = 1.425\;\lambda = -4478.22\).

By replacing the encoded \(x_1\) and \(x_2\) variables with natural \(x_1\) and \(x_2\) variables, the results standing for the optimum parameters are:

I. For \(\hat{y} = 10000\), \(\hat{z}_1 = 79.417^\circ C\); \(\hat{z}_2 = 6.345\;\)h.

II. For \(\hat{y} = 9000\), \(\hat{z}_1 = 79.42^\circ C\); \(\hat{z}_2 = 6.425\;\)h.
Error calculation in process performance ($\delta$) was evaluated by computing the following data: average variance, coefficients variance and distribution values of the process performance.

The error calculation for the two considered optimum regimes has led to the following final results:

I. $\bar{y} = 10000$, $\delta_y = 9.056 \cdot 10^{-3} \cdot s_y = 2.179 \cdot 788.514 = 1718$.

II. $\bar{y} = 9000$, $\delta_y = 9.056 \cdot 10^{-3} \cdot s_y = 2.179 \cdot 879.979 = 1917$.

Thus, as the process is performed under the best evaluated parameters, the molecular weights of the collagen hydrolysate components will stand in the limits of $\bar{y} - \delta_y < M < \bar{y} + \delta_y$.

The experimental checks of the best alkaline hydrolysis conditions at the atmosphere pressure, pinned down through mathematical simulation, such as a temperature of 79.4°C and a time of 6.4 h have been validated by obtaining a collagen hydrolysate with an average molecular weight of 8400 Da.

The major characteristics determined for the collagen hydrolysate obtained under optimal hydrolysis conditions are presented in table 5. The average molecular weight was determined by Sörensen method and polyacrylamide gel electrophoresis (fig. 1).

Another objective of the advanced hydrolysis of chrome leather wastes was to release amino-acids, known as useful additives involved in the plant metabolism, particularly under climate stress conditions [9]. Amino-acid composition in the protein hydrolysates was determined by High Performance Liquid Chromatography, and it is presented in table 6.

Obtaining new foliar biofertilizers containing protein additives, intended to be used in stimulating the plant growth

Our previous papers concerning the foliar nutritive products, which are diluted hydrolyzing emulsions, have shown that most of foliar properties are carried out by the aliphatic acid overbasic salts [10]. Particularly, potassium overbasic naphthenates with molar ratio KOH/naphthenic acids 4/1 exhibit not only the best properties as foliar fluids (complete water solubility, adherence, hiding power, moderated alkalinity, penetration power through plasma cell membrane, compatibility with hard waters used for dilution), but also the adequate capacity to accommodate different NPK formulas and additives without major changes in their properties like density, viscosity and surface tension. More than that, potassium overbasic naphthenates are themselves good growth enhancers. Unexpectedly, potassium overbasic naphthenates emulsions with concentration 1mol/L (in terms of KOH) do not mix in all proportions with collagen hydrolysates, probably due to high concentrations in mineral salts. Limited solubility of collagen hydrolysates reduces the variability of amino-acid concentrations in nutritive fluid formulations. Nevertheless, some particular formulations containing 2 mol/L urea and usual concentrations and ratios in micronutrients are stable emulsions and might be considered true dilutable concentrate products suitable for foliar application after dilution. Two of these formulations are given in table 7.

The composition of these products, as a matter of fact, derives from the same intermediaries previously described [10], whose main attributes are hydrolysis after dilution with water up to ratio 1/100, and formation of an adherent layer on the foliage surface. Because the overbasic potassium naphthenate 4/1 emulsion makes up more than 8/10 from the mass of the two foliar products (table 7) it is rational to regard these products as fluids with similar behaviour on application on the plant leaf as the originating potassium naphthenate emulsion. Actually, we may easily demonstrate that the layout of leaf adherent semisolid film starts with potassium overbasic naphthenates hydrolysis, continue with the carbonation and precipitation the inorganic amorphous aggregates overlapping the organic hydrolysates layer and comes to an end with the partial evaporation of the liquid phases. Preliminary partial carbonation or neutralization is a simple and ready to use way to control the hydrolysis pH to values prove to be non harmful for foliage. All the chemical species born in semisolid hydrolyzing film on the foliage surface are able to easily penetrate cuticular membranes at high rate and nutrient/growth enhancer best predicted ratios. Figure 2 describes accurately the mechanism of foliar film formation and backs up the similarity of the film formation when intermediary overbasic potassium naphthenate or products 1 and 2 are applied on the leaf. According to this figure we may assume that immediately after application the emulsified overbasic salts hydrolysis advances due to air free carbon dioxide absorption and the liquid film breaks out in a discontinuous micelle structured layer of organic hydrolysates. Also, the carbonation process and water

---

**Table 5**

<table>
<thead>
<tr>
<th>Collagen hydrolysate</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids %</td>
<td>Total ash %</td>
</tr>
<tr>
<td>H1</td>
<td>4.04</td>
</tr>
</tbody>
</table>

*values based on the solids, ** determined by Sörensen method.

**Table 6**

<table>
<thead>
<tr>
<th>Amino-acid</th>
<th>Glycine</th>
<th>Aspartic acid</th>
<th>Glutamic acid</th>
<th>Serine</th>
<th>Histidine</th>
<th>Tyrosine</th>
<th>Proline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount, %*</td>
<td>0.320</td>
<td>0.033</td>
<td>0.043</td>
<td>0.043</td>
<td>0.057</td>
<td>0.023</td>
<td>0.240</td>
</tr>
</tbody>
</table>

* based on the hide substance.
evaporation promote inorganic phase nucleation and growth over the hydrolysates layer as far as a significant decline in liquid phase pH takes place. Minimum value of $pH$ is reached when full hydrolysis is achieved and organic matrix layer building up ceased. Further water evaporation may raise eventually the hydroxyl concentration in liquid phase as it is presented in figure 2, but this scenario is certainly non valid when foliar absorption proceeds simultaneously with hydrolysis and carbonation.

Efficiency of these foliar biofertilizers was tested through trials on tomatoes and aubergines according to standard procedures accepted for the evaluation and homologation of new products for agricultural use. The trials have shown that the 10-50% increase in production is accompanied by significant raise in quality when products 1 and 2 have been applied in suitable doses during the three main stages of plant growth.

Obtaining biofuels from hide wastes

Fatty matters were extracted from the hide wastes by an adequate solvent. Fat content in wastes is critical for separation efficiency and chemical conversion yield. Extractable fatty matters are further catalytically transesterified into fatty acid methyl esters (FAME), which after purification and drying have been characterized as common biofuels for heating (table 8).

Extraction of fatty matter from the hide waste was achieved with two types of solvent: $n$-heptane and biodiesel [15]. The chemical composition of the fats transesterification products in the above named solvents is given in the table 8. The hide recovered fats are carrying their own distribution of fatty acids in terms of molecular weights and number of double bonds. This distribution is genuinely reflected in composition of FAME when $n$-heptane is used as extraction solvent. Consequently, in the resulting biofuel the fatty acids mass ration $C_{18}/C_{16}$ is almost 2/1, very close to the same ratio in the recovered fats from the hide wastes. In the biodiesel obtained from the sunflower oils the contribution of $C_{18}$ acids is almost 93%.

The difference in fatty acids distribution makes mainly the differences in biofuels physical and combustion properties (table 9). Accordingly, fat extraction with $n$-heptane resulted in FAME with the pour point 10°C which is improper for its use as heating biofuel (standard EN 14213). Replacing $n$-heptane with biodiesel as fat extractant from the hide wastes and carrying our the transesterification reaction in this solvent changes not only the product composition and combustion properties, but also significantly lowers the energy expenditure, as far as no

<table>
<thead>
<tr>
<th>Component</th>
<th>Foliar product 1</th>
<th>Foliar product 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/1 partly carbonated overbasic potassium</td>
<td>-</td>
<td>0.68</td>
</tr>
<tr>
<td>naphthenate, mol/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/1 partly neutralized overbasic potassium</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>naphthenate, mol/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protein hydrolysate H1, g/l</td>
<td>170.7</td>
<td>172.3</td>
</tr>
<tr>
<td>Urea, mol/l</td>
<td>2.22</td>
<td>2.26</td>
</tr>
<tr>
<td>Ethanolamine, mol/l</td>
<td>0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>Boron, g/l</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Zinc, g/l</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Cuper, g/l</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Molybdenum, g/l</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 7

COMPOSITION OF THE FOLIAR PRODUCTS INTENDED TO BE USED IN PLANT BIOFERTILIZATION

Table 8

FATTY ACID COMPOSITION OF BIOFUELS

<table>
<thead>
<tr>
<th>Fatty acids (number of carbon atoms: number of double bonds), mass %</th>
<th>Biodiesel</th>
<th>FAME in fatty matters ($n$-heptane as solvent)</th>
<th>FAME in fatty matters (biodiesel: fat ratio 1:1)</th>
<th>FAME in fatty matters (biodiesel: fat ratio 2:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14:0</td>
<td>0.20</td>
<td>2.84</td>
<td>1.69</td>
<td>1.14</td>
</tr>
<tr>
<td>C16:0</td>
<td>6.29</td>
<td>31.40</td>
<td>18.12</td>
<td>13.83</td>
</tr>
<tr>
<td>C16:1</td>
<td>0.93</td>
<td>0.36</td>
<td>0.20</td>
<td>0.56</td>
</tr>
<tr>
<td>C18:0</td>
<td>4.03</td>
<td>17.89</td>
<td>10.84</td>
<td>8.45</td>
</tr>
<tr>
<td>C18:1-﻿trans</td>
<td>0.76</td>
<td>1.96</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>C18:1-﻿cis</td>
<td>25.31</td>
<td>43.54</td>
<td>29.47</td>
<td>28.65</td>
</tr>
<tr>
<td>C18:2-﻿trans</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18:2-﻿cis</td>
<td>62.48</td>
<td>1.42</td>
<td>38.98</td>
<td>47.37</td>
</tr>
<tr>
<td>C18:3n6</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18:3n9</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Fig.2. Layered matrix precipitation. Diluted solutions 1/100. Neutralized intermediate pH 10 (□); Non-neutralized intermediate pH 12.2 (■); Foliar Product 1 (○); Foliar Product 2 (▲)
solvent has to be removed, and moreover the methanolysis takes place at the room temperature in a very short time. It could be noticed from table 8 that some minor components found in the n-heptan methanolysis product are missing from the biofuels produced at both 1:1 and 2:1 ratios biodiesel/fat extraction and methanolysis. Therefore, the change of solvent certainly amends the rates of main transesterification reactions at secondary undesired reactions expense. As the result, the increase in ratio biodiesel: fat displaces the pour point of FAME products from 10°C to 4°C and respectively 0°C (table 9). These new FAME products are adequate for use as biofuels in heating plants or as diesel biofuels (EN 14214:2003).

The protein remained after fat extraction and the remaining hide wastes with low fat content was subjected to an alkaline hydrolysis, resulting in a product containing protein hydrolysates and fatty acid salts (alkaline soaps) proper to be used as an additive for hydraulic cements, mortars and concretes, particularly for improving the mechanical strengths, the workability and for reducing sweating and segregation [18].

Conclusions

Obtaining additive and advanced biomaterials from resources consisting of tannery protein by-products is a new approach of the subject which may lessen the pressure of a significant environmental issue. The work has revealed the possibility of optimizing the process parameters for the chemical hydrolysis of chrome tanned leather wastes at the atmosphere pressure. A mathematical simulation program was concluded with the best reaction parameters for complete separating of the chromium compounds and protein conversion into peptides and amino-acids carrying plant growth stimulants and enhancers. It was shown the alkaline hydrolysis of chrome tanned leather wastes at 79.4°C for 6.4 h results in chromat free collagen hydrolysate containing peptides with mean molecular weight of 8400 Da, a mixture of free amino-acids (glycine, aspartic acid, glutamic acid, serine, histidine, tyrosine and proline) and salts. Collagen hydrolysate was used for new foliar biofertilizers and growth enhancers formulations. It was demonstrated that these formulations exhibit appropriate properties, typical for foliar application, as stability, viscosity, surface tension, hiding power, adherence as well as nano-dimensional hydrolysate particles, which enables slow release into leaf metabolites and high efficiency due to the fast and complete penetration through plants cuticular membranes.

Residual fatty matters originating from bovine hide were converted into all-purpose heating biofuels applying a new procedure of extraction of fat from hide wastes contaminated with organic and/or inorganic impurities and further processing by methanolysis. The novelty of the process consists in the use of biodiesel as extraction solvent, which is cheap, does not require the distillation recovery and enriches the characteristics of finished product, particularly the viscosity, cold filter plugging and pour point. Biofuel obtained from the methanolysis of 1:2 tallow biodiesel mixture with a pour point 0°C can be used both as a biofuel in heating plants or biodiesel, complying with the requirements of EN 14213 and EN 14214 standards.

The paper provides fair solutions for the total reclamation of hide wastes by common conventional processes and technologies relevant for the lessening of leather manufacture environmental impact.

Acknowledgment: The work was carried out with the financial support of the Excellence Research Program, within the project 252/2006 and CAPACITATI Program, bilateral cooperation Romania-Turkey project.

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Manuscript received: 7.05.2008

REV. CHIM. (Bucureºti) • 60 • Nr. 5 • 2009