

Equipment and technology for treating the limed fleshings resulted from bovine hide processing

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Wastes known as „limed bovine fleshings” are the result of the bovine hide fleshing by means of fleshing machines equipped with special knives, following the hide liming. Hides resulted from fleshing machine are almost invariable in thickness and are directed to tanning with chromium salts. The resulted wastes – „limed bovine fleshings”- are small limed hide pieces with no grain, **consisting particularly of collagen protein and bovine fat (suet), and 80-85% water**. They are bulky with only 12% dry solids, and because of the residual calcium hydroxide in the interstitial water, they are highly alkaline of pH 11-12, and noxious.

Most of the „limed bovine fleshings” result from bovine hide processing, accounting for 14-17% of the raw hide weight. Their storage is a hard question, and in view of the accession to EU, the leather manufacturers in Romania have to solve the issue of organic waste disposal.

Therefore, our Institute together with other institute and S.C.TAMIV S.A. Brasov dealt with the treatment of such wastes by **hydrolysis** which has resulted in non-noxious in-process materials: **collagen hydrolysate and bovine fat (suet)**. Collagen hydrolysate could be used in hide processing and in agriculture as fertilizer, and suet could be used as such in hide processing.

Calcium is previously removed by means of some salts able to do this, like as ammonium sulphate or ammonium chloride – **operation known as deliming**, thereafter the interstitial water imparts the wastes a neutral pH (7-7,5); thermal hydrolysis was performed in an enameled steam apparatus with a stirrer, charging holes for water and wastes, thermometer and pressure meter.

The benefit of this process is the conversion of noxious wastes in one or more non-noxious materials useful in the agriculture and tanneries, thus being returned to the economy cycle.

I. INTRODUCTION

Wastes resulted from hide processing, after the liming operation, by means of fleshing machines in order to obtain a pelt level in thickness are known as „limed bovine fleshings” or „limed flesh”.

So far, all tanneries in our country have been disposing the above wastes into the refuse pits in the locality neighbourhood. As in 2007 Romania is to access to the EU, the tanneries must to solve the process wastes according to the European regulations in force.

Formerly, the limed bovine fleshings were used exclusively in making glue, but nowadays, with the development of acryl-, polyurethane- and latex-based binders, the glue is not required any more.

Under these circumstances an original process was thought and experienced, where the limed bovine fleshings are treated with one of the 3 investigated deliming agents (35 % ammonium sulphate, ammonium chloride or hydrochloric acid) aimed to remove calcium and

saponification reaction, respectively, resulting in such by-products as **collagen hydrolysate** and **suet** used in leather industry and agriculture.

II. EXPERIMENTAL

To process the lime bovine fleshings, sampling was carried out from several batches 16-30 kg weight pelts, the samples were subject to chemical-physical tests, and the results are shown in Table 1.

Table 1. Chemical-physical tests for limed and delimed bovine fleshings

Ref. No.	Characteristic	Values	
		Values for limed bovine fleshings	Values for delimed bovine fleshings
1.	Appearance	Heterogeneous product made of gelatin and fat particles soaked with water.	Heterogeneous product made of gelatin and fat particles soaked with water.
2.	Colour	Grey	White
3.	Smell	Odourless in the first 48-60 hours at the room temperature, thereafter getting a characteristic smell of decaying protein.	Odourless in the first 48-60 hours at the room temperature, thereafter getting a characteristic smell of decaying protein.
4.	Moisture content, %	80 – 85%	53.00 – 72.00
5.	Ash, %	13.00 – 15.00*	2.50 – 15.00*
6.	Fatty matter, %	9.00 – 15.00*	4 – 11.50*
7.	Total nitrogen, %	12.00 – 14.00*	3.00 – 11.50*
8.	Hide matter, %	70.00 – 80.00*	40.00 – 62.00*
9.	Calcium oxide, %	6.00 – 10.00*	1.00 – 2.50*
10.	Sodium sulphide, %	2.00 – 4.00*	2.50 – 9.50*
11.	pH	10.5 – 12.5	7.5 – 8.0

* Values are based on the water-free weight

Frame process for limed bovine fleshings hydrolysis

In order to process limed bovine fleshings, a plant was build in S.C.TAMIV S.A. Braşov, involving a BERG pump, collecting the fleshings from the fleshing machine and feeding them into the deliming drum - a 2500 l liming drum, two 2000 l autoclave and a 1500 l homogenizing vessel, as shown in the flow chart.

1. Collecting the fleshings and feeding them into the deliming drum

This operation is performed by means of a BERG pump.

2. Deliming - performed in the liming drum

Material:	1 000 kg limed bovine fleshings from 16-20 kg or 25-30 kg weight pelts	
Washing I:	water at 30°C, 200 % 30 minutes	The bath is sampled – sample 1
Washing II:	water at 30°C, 200 % 30 minutes	The bath is sampled – sample 2
Deliming:	water at 30°C, 200 % + (NH ₄) ₂ SO ₄ , 20 kg 60 minutes	The bath is sampled – sample 3
	+ (NH ₄) ₂ SO ₄ , 10 kg 60 minutes	The bath is sampled – sample 4
	+ (NH ₄) ₂ SO ₄ , 10 kg 60 minutes	The bath is sampled – sample 5
	+ (NH ₄) ₂ SO ₄ , 10 kg 60 minutes	The bath is sampled – sample 6
	+ (NH ₄) ₂ SO ₄ , 10 kg 60 minutes	The bath is sampled – sample 7
Final washing:	water at 30°C, 200 – 300 % 25 – 20 minutes	The bath is sampled – sample 8

The bath sampling was aimed at checking the deliming process and final pH and the chemical load in the deliming bath. Longer deliming times and higher amount of (NH₄)₂SO₄ have resulted to be required for the limed bovine fleshings originating from 25-30 kg weight pelts in order to achieve a pH of 8.0

Deliming has been completed when two requirements are met:

- a sample of the above fleshings gets a redish-purple colour when tested with an alcoholic solution;
- deliming bath pH is 8.0 – 7.5.

3. Hydrolysis

This operation is carried out in the 2 000 l autoclave, at 100 – 125 °C, 2.0 – 2.8 bar pressure for 10-12 hours, resulting in two products: collagen hydrolysate and suet, which characteristics are shown in Tables 2 and 3, respectively.

Bovine fleshings hydrolysis was conducted in an neutral medium when “neutral collagen hydrolyzate” was intended to be obtained to be used as fertilizer in the agriculture, and in an acid medium when products used in hide processing were intended to be obtained, like as: fillers and adhesives used in pasting.

Table 2. Chemical-physical characteristics of the half-prepared product ‘neutral and acid collagen hydrolysate’ obtained from limed bovine fleshings delimed with $(\text{NH}_4)_2\text{SO}_4$

Ref. No.	Characteristic	Values	
		Collagen hydrolysate from fleshings	
1.	Appearance , colour, smell	Dark brown collagen protein solution	Dark brown collagen protein solution
2.	Dry matter, %	8.00 – 13.00%	7.50 – 9.50
3.	Ash, %	7.00 – 9.00*	5.35 – 13.33*
4.	Total nitrogen, %	14.00 – 16.00*	13.46 – 10.26*
5.	Protein nitrogen, %	13.00 – 15.00	12.50 – 9.60*
6.	Hide matter, %	73.00 – 87.00*	70.00 – 54.00
7.	Ammonia nitrogen, %	1.00 – 1.50*	0.98 – 0.65*
8.	Amine nitrogen, %	0.50 – 0.70	0.42 – 0.35*
9.	Fatty matter, %	1.50 – 3.00*	10 – 13.00*
10.	Calcium oxide, %	2.50 – 3.00*	3.50 – 5.60*
11.	Sodium sulphide, %	0.50 – 3.00*	5.47 – 11.25*
12.	pH	8.0 – 7.5	4 – 5
13.	Shelf life	7 days in cold seasons and 2-3 days in summer	
14.	Molecular weight: daltons	About 70 000	b- 15 000 – 30 000

- Values are based on the dry weight

Table 3. Chemical-physical characteristics of the by-product suet obtained from bovine fleshings

Ref. No.	Characteristic	Values
1.	Appearance, colour, smell	Solid fatty product, of yellow-brownish colour, with a characteristic smell of bovine fat
2.	Solids, %	80.0, min.
3.	Fatty matter, %	90.0, min.*
4.	Iodine number, g/100g	45...55
5.	Saponification number, mg KOH/g	190...200
6.	Melting point, °C	40...45
7.	Specific gravity, g/cm ³	0.92-0.95
8.	Shelf life	6 months in the cold seasons 3 months in summer

* The value is based on moisture-free weight

4. Establishing the consumptions of materials and utilities for the treatment of 1 000 kg limed bovine fleshings

4.1. Consumption of auxiliary materials

For deliming 1 000 kg of limed bovine fleshings a varying amount of $(\text{NH}_4)_2\text{SO}_4$ is required, according to the fleshing origin, as follows:

- for fleshings resulting from 16 – 20 kg weight pelts, 60 kg of $(\text{NH}_4)_2\text{SO}_4$ is required
- for fleshings resulting from 25 – 30 kg weight pelts, 80 kg of $(\text{NH}_4)_2\text{SO}_4$ is required

The average consumption is of 70 kg $(\text{NH}_4)_2\text{SO}_4$ /1 000 kg fleshings.

4.2. Water consumption

By summing the water amount required in delimiting has resulted a consumption of 3 m³; in hydrolysis a further amount of 0.5 m³ is required; to wash the equipment 0.5 m³ water is required, therefore amounting about 4 m³.

4.3. Steam consumption

It was estimated at 0.5 Gcal /1 000 kg fleshings.

4.4. Power expenditure

The power required by engine driving the 2000 l autoclave is of 3.5 kWh, working 10 hours/batch of hydrolysed limed bovine fleshings

5. Resulted products

The by-product amounts resulted from 1 000 kg limed bovine fleshings:

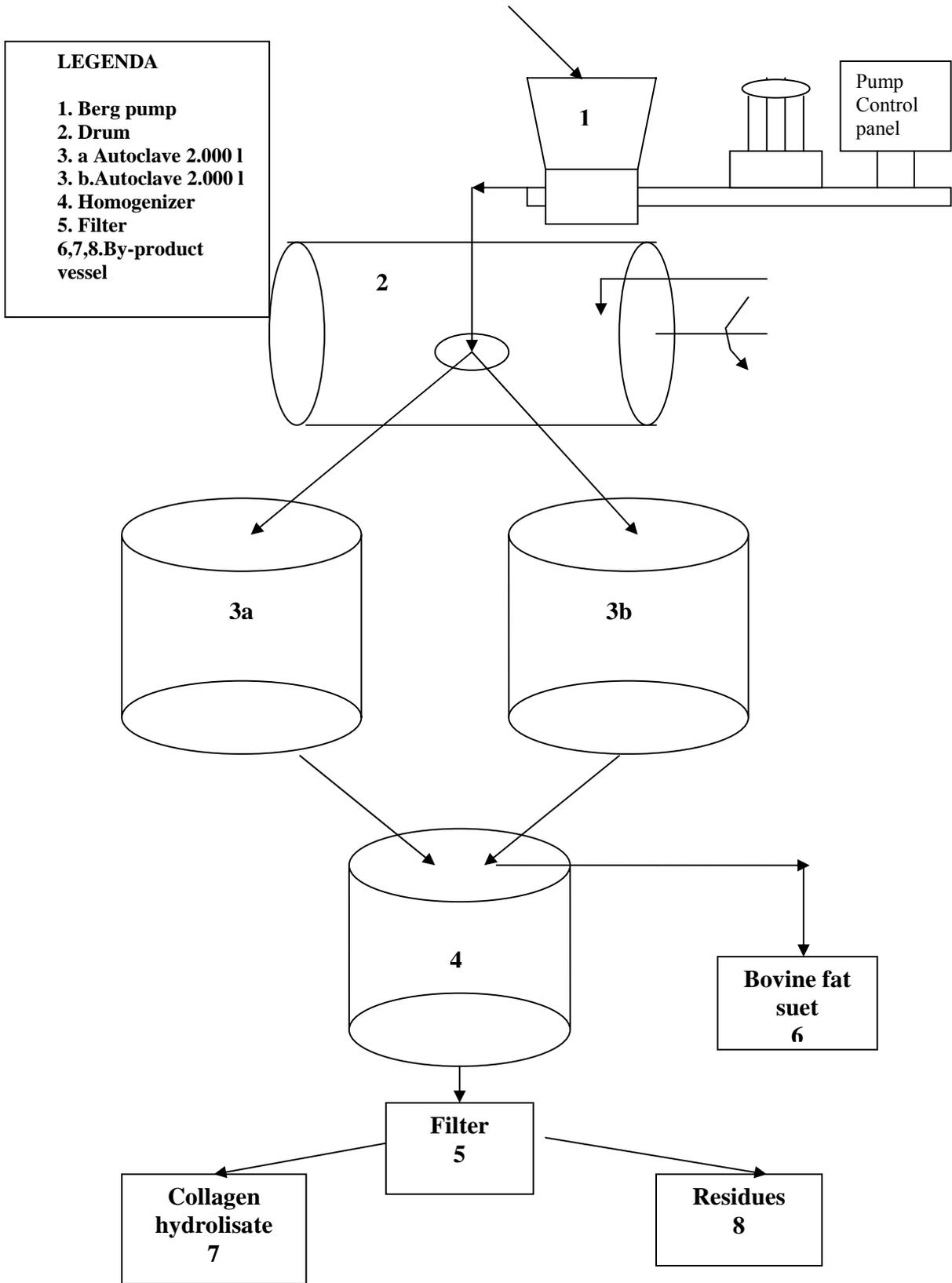
1. 800 kg collagen hydrolysate (neutral or acid), which can be used as fertilizer in farming, and as a filler and retanning agent in leather manufacture, after a previous chemical treatment;
2. 30 kg suet, which can be used in fatliquoring leather intended for harness;
3. 170 kg residues, which can be used as fertilizer, being applied before autumn ploughing, or disposed to the refuse pit in the locality neighbouring;
4. From the collagen hydrolyzate resulted from acid hydrolysis with hydrochloric acid, a collagen hydrolyzate with a low molecular weight (15000 – 30000) was obtained and subsequently modified chemically by grafting it with acrylic monomers, as follows:
 - 4.1 by grafting with ethyl acrylate, a deacidifying-filling-retanning agent has been obtained and used with good results in protected chrome bovine splits;
 - 4.2 by grafting with acrylamide, an adhesive product was obtained and used with good results in pasting the protected chrome bovine splits onto the plates.

CONCLUSIONS

As a result of the experienced process and putting into service the pilot plant for reclaiming the lime bovine fleshings, the process variables have been established as follows:

1. Delimiting 1 000 kg of lime bovine fleshings is performed in a liming drum (as shown the flow chart) at 20 rpm, in which 60-80 kg delimiting agent-ammonium sulphate are added gradually for 6 -8 -10 hours, according to the pelt weight the fleshings come from: 16-20 kg or 25 – 30 kg. NH₄Cl was also tried with good results in delimiting the bovine fleshing.
2. Hydrolysis
1 000 kg of delimited bovine fleshings, with a pH value of 8.0- 7.5, were fed to the autoclave, and the large pieces were cut; hydrolysis took place at 120°C and a pressure of 2.5 – 2.8 bar for 10 hours.
3. Separation of the products resulted from hydrolysis
From the hydrolysis have resulted two by-products and the residue as a waste, as follows:
 - 3.1. collagen hydrolysate: a) neutral, which is could be used as fertilizer
 - b)acid, modified chemically by grafting with acrylic monomers, ethylacrylate and acrylamide, which could be used auxiliary material in filling leather, and pasting them onto the plates;

- 3.2. bovine fat, known as suet, which can be used in tanneries in fatliquoring leather intended for harness, and in soap industry;
- 3.3. residues, which can be disposed as a refuse or used as fertilizer applied under the furrow in autumn ploughing.



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