Adding Value to Tannery Fleshings: Part I – Oils and Protein Hydrolysates – Production and Application

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Summary

The tanning industry generates a high quantity of solid wastes. Therefore, there is a need to create valorization [added value] options for these wastes. The present work had as its main objective creating added value by production of fat and hydrolyzed protein. To this end, fleshings were treated by hydrolysis with regard to the influence of various factors. The best result was found for a temperature of 60°C, 4 hours of hydrolysis, 2% of enzyme and 100% of water, with a fat extraction yield of 93%.

The fat obtained through the hydrolysis process was used to produce sulphated oils. The protein hydrolysate was concentrated to about 40% of solids content and used to prepare co-products of protein hydrolysate and glutaraldehyde.

Sulphated oils were applied in leather fatliquoring and the different protein hydrolysates were tested in leather retannage. The leather samples obtained were evaluated by physical-mechanical tests and the results were compared to those obtained through a standard process. The results were very satisfactory and, in some cases better than the specified standard.

The process of adding value to this waste results in a double advantage for the leather industry, reducing the environmental impact and allowing production of alternative products for leather fatliquoring and retannage.

1. INTRODUCTION

The tanning industry generates a high quantity of solid wastes of a polluting nature. It is known that only 20% of the hide results in finished products.[1] Considering the economical and environmental points of view, there is a great interest in the valorization [adding value to] of the generated solid wastes. Lime fleshings from hide fleshing amount to an estimated quantity of 40 ton per day in Portugal (data from CTIC – Portuguese leather centre). This kind of solid waste is an important fat source, normally disposed off or treated. Composting to obtain fertilizers, anaerobic digestion to produce energy and fat extraction, are, among others, the most important treatments.[2-7, 12-14]

Enzymatic treatment of fleshings by hydrolysis[4] is one way for fat extraction. The hydrolysis produces fat, as the main product,[7] and a protein hydrolysate.

Leather treatment comprises, amongst various processes and mechanical operations, two that are related to this study: fatliquoring and retannage. Fatliquoring is a process used to improve leather's softness and mechanical strength by the use of oils and lubrication resins. Retannage is a process used to improve roundness, grain firmness and leather filling by the use of vegetable tannins, syntans and various types of resins.

The fat obtained from fleshings hydrolysis can be used to produce oils, by sulphation, for fatliquoring of leather,[4] or to obtain biodiesel.[8,9] Some work has been published on the use of collagen hydrolysates obtained from chrome shavings[10,11] to develop products for leather retannage.

This work intends to study fleshings hydrolysis in order to obtain two products: fat and protein hydrolysate. The fat is used to produce oils for leather fatliquoring and the protein hydrolysate is used to develop products for leather retannage.

2. MATERIALS AND METHODS

Fleshings, obtained from domestic hides, were first crushed and then characterized for moisture, mineral and organic matter content, fat and protein content.[15]

2.1 Fat extraction

Crushed fleshings were treated by thermal and/or enzymatic hydrolysis. Fleshings hydrolysis was studied regarding the influence of various factors such as the amount of enzyme and water needed, temperature and contact time.

The hydrolysis procedure was: 50g of ground fleshings were mixed in a 250ml flask with a certain amount of water and enzyme, ERHA PH3895, a protease from TFL active at pHs between 10 and 13 and designed to dissolve collagen. The flask was shaken in a thermostatic water bath at the desired temperature for the intended extraction time. After

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hydrolysis, the mixture was left to cool overnight for separation of the three phases. Most of the upper phase, the fat phase, was separated with the aid of a spatula. The remaining mixture was centrifuged for the separation of the solid phase. Because the liquid phase (hydrolysate) still contained some fat, it was filtered to remove it. The total fat phase was dried at 80°C in an oven to constant weight and the fat content was evaluated. The solid phase was dried too. The water and enzyme amounts, temperature and contact time used are shown in Table I for each trial done.

TABLE I
Hydrolysis trials carried out for the study of enzyme effect

Water (%)[1]	Enzyme (%)[1]	Temperature (°C)	Time (h)
100	0.25 0.50 0.75 1.00 2.00	60	2, 4 and 6

[1] % based on fleshings weight

TABLE II
Hydrolysis trials carried out for the effect of water amount

Water (%)[1]	Temperature (°C)	Time (h)
0 50 100 150	60	6

TABLE III
Hydrolysis trials carried out for the effect of time

Water (%)[1]	Temperature (°C)	Time (h)
100	60	2 4 6

TABLE IV
Trials at a larger scale in the PARR reactor

Trial	Fleshings (g)	Water (%)	Enzyme (%)	Time (h)	Temperature (°C)
A			2		60
B	300	100	0	4	90

Table II shows the amount of water, temperature and contact time used for the study of the effect of water volume (no enzyme was used in these trials). These trials were repeated for 70, 80 and 90°C.

In order to evaluate the influence of hydrolysis time, three trials were done in the conditions shown in Table III. These trials were repeated at 70, 80 and 90°C.

The conditions that led to the best results: 60°C, 4 hours contact time, 100% of water and 2% of enzyme, shown in Table IV as trial A, were used to produce fat and protein hydrolysate at a large scale using a PARR reactor in order to obtain a greater quantity of fat and protein hydrolysate for the production of oils and hydrolysate products. Another trial was made (trial B) using the best conditions without enzyme.

2.2 Oil production

Fat obtained from the two tests represented in Table IV were joined and purified with n-hexane. This fat was characterized by acid, saponification and iodine values and used to produce sulphated oils using different amounts of sulphuric acid.

The procedure was: different amounts of sulphuric acid were added slowly to 10g of fat with cooling, when necessary, to maintain the temperature below 50°C; the mixture was left to stand for two hours and then pH was adjusted with a sodium hydroxide solution to values between 5 and 6; the mixture was then washed with an aqueous solution of sodium chloride (10% w/w). Four oils were produced, S1, S2, S3 and S4, with different amounts of sulphuric acid: 1, 2, 3 and 4g respectively as shown in Table V.

TABLE V
Amounts of fat, sulphuric acid and sodium hydroxide solution used in oils production

Oils	Fat (g)	H_2SO_4 (g)	NaOH 30% (g)
S1	10.1678	1.0050	2.5186
S2	10.3452	2.0050	5.0580
S3	10.4444	3.0083	7.5390
S4	10.2597	4.0543	10.0377

TABLE VI
Amounts of HP and glutaraldehyde used in production of the different GHP

GHP	HP (g)	Glutaraldehyde (%)	Glutaraldehyde weight (g)
GHP11	3.6004	11.5	0.4133
GHP34	3.7606	33.6	1.2630
GHP50	5.0147	50.0	2.5084
GHP100	4.0371	99.5	4.0174

TABLE VII
Summary of fatliquoring and retanning trials, 1.8 mm thickness leather samples

Trial	Chemical tested	Description
G	–	Usual chemicals were used
G1	Oil S1	Oil S1 replaced the usual sulphated oil (Indinol T)
G2	Oil S2	Oil S2 replaced the usual sulphated oil (Indinol T)
G3	Oil S3	Oil S3 replaced the usual sulphated oil (Indinol T)
G4	Oil S4	Oil S4 replaced the usual sulphated oil (Indinol T)
G5	HP	HP was used replacing a dicyanodiamide resin (Fortan DC)
G6	HP	HP was used replacing an acrylic resin (Fortan A40)
G7	GHP50	GHP50 was used replacing an acrylic resin (Fortan A40)
G8	GHP100	GHP100 was used replacing an acrylic resin (Fortan A40)

* Fortan DC, Fortan A40 and Indinol T are chemicals from a Portuguese chemical company (INDINOR)

TABLE VIII
Summary of fatliquoring and retanning trials, 1.2 mm thickness leather samples

Trial	Chemical tested	Description
T	–	Usual chemicals were used
T1	Oil S1	Oil S1 replaced the usual sulphated oil (Indinol T)
T2	Oil S2	Oil S2 replaced the usual sulphated oil (Indinol T)
T3	Oil S3	Oil S3 replaced the usual sulphated oil (Indinol T)
T4	Oil S4	Oil S4 replaced the usual sulphated oil (Indinol T)
T5	HP	HP was used replacing a dicyanodiamide resin (Fortan DC)
T6	HP	HP was used replacing an acrylic resin (Fortan A40)
T7	GHP11	GHP11 was used replacing an acrylic resin (Fortan A40)
T8	GHP34	GHP34 was used replacing an acrylic resin (Fortan A40)
T9	GHP50	GHP50 was used replacing an acrylic resin (Fortan A40)
T10	GHP100	GHP100 was used replacing an acrylic resin (Fortan A40)

* Fortan DC, Fortan A40 and Indinol T are chemicals from a Portuguese chemical company (INDINOR)

2.3 Hydrolysate treatment

The protein hydrolysate, obtained by the addition of the hydrolysates from the two PARR tests, was characterized for solids, kjeldahl nitrogen, mineral and organic matter content. Its pH was adjusted to 6 with formic acid, and then it was concentrated by evaporation to 40% of solids content. This protein hydrolysate, with 40% of solids content, was designated as HP.

In order to increase its molecular size and reactivity, HP was treated with different amounts of glutaraldehyde (30% conc.) and shaken for one hour at room temperature. Glutaraldehyde amounts varied between 11 and 100% (% based on the HP weight). The mixture prepared with 11% of glutaraldehyde was designated as GHP11, and similarly for other GHP preparations as shown in Table VI.

2.4 Leather treatment and evaluation

The evaluation of the effects of the oils and hydrolysates in leather fatliquoring and retannage was done using shaved wet-blue with two different thicknesses: 1.2mm and 1.8mm. Two standard processes with the usual oils and retanning agents were made for each thickness, process T for 1.2mm and process G for 1.8mm. These processes were changed replacing the usual oils and retanning resins by the oils and hydrolysate products obtained from the fleshings. Tables VII and VIII show a summary of the trials that were made for 1.8mm and 1.2mm thicknesses.

These trials were done at a bench scale with small pieces of wet-blue, weighing about 80g. After the treatment, the leather pieces were dried, staked and submitted to physical-mechanical tests according to ISO 3377:2002 for tear strength and ISO 3379:1976 for ball burst test (to evaluate the grain cracking).

3. RESULTS AND DISCUSSION

First, crushed fleshings were characterized. Table IX shows the characterization results for one lot of fleshings obtained from processing domestic hides.

TABLE IX
Fleshings characterization

Parameter	Results
Moisture (%)	70.1
Mineral matter (% dry basis)	10.7
Organic matter (% dry basis)	89.3
Fat content (% dry basis)	58.3
Protein content (g protein/100g of fleshings)	4.1

TABLE X
Results of the extraction process in large scale

Trials	Hydrolysate obtained (g)	Solids content of hydrolysate (%)	Fat extraction yield (%)
A	434.63	5.86	68.3
B	386.91	4.25	56.1

3.1 Fat extraction

Ground fleshings were treated in order to study the influence of various factors on hydrolysis: the amounts of enzyme and water, temperature and time. Figures 1, 2 and 3 show the effect of these factors. For each trial, the fat extraction yield was calculated as the weight ratio of dry fat obtained to fleshings fat content, on a dry basis.

The results obtained show that temperature and enzyme are the more important factors to be considered. The results in Figures 1, 2 and 3 show that it is possible to conclude that the best result was obtained for 60°C, 4 hours contact time, 100% of water and 2% of enzyme addition. These conditions appear to be the best option because temperature is only 60°C, reducing the energy cost of the extraction process. An economical study is important to compare the costs of energy and enzyme. The extraction process was repeated at a larger scale, the results are shown in Table X.

Against the expected, the fat extractions yields (%) are lower than that obtained in the trials for the same conditions with 50g of fleshings.

3.2 Oil production

The characterization results of fat used in oils production and of the oils produced are shown in Tables XI and XII.

Considering the SO_3 results and checking the literature,[16,17] it can be said that oils S1 and S2 were slightly sulfated, oil S3 was moderately sulfated and oil S4 was strongly sulfated.

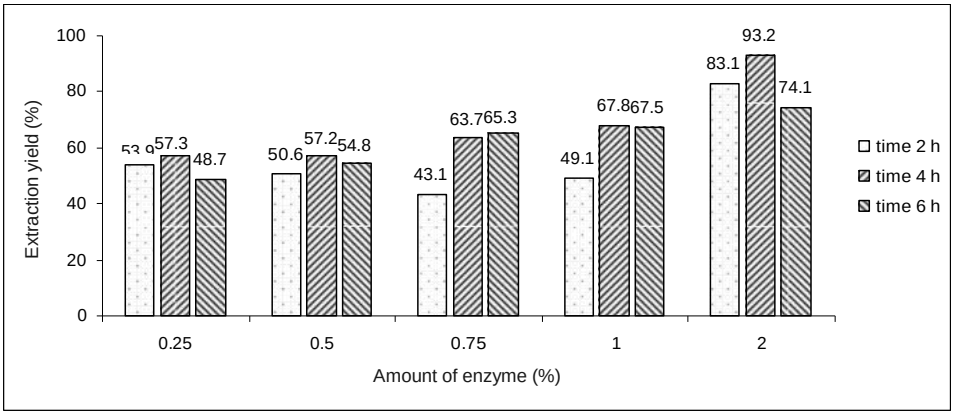

Figure 1. Fat extraction yield *versus* amount of enzyme and contact time at 60°C.

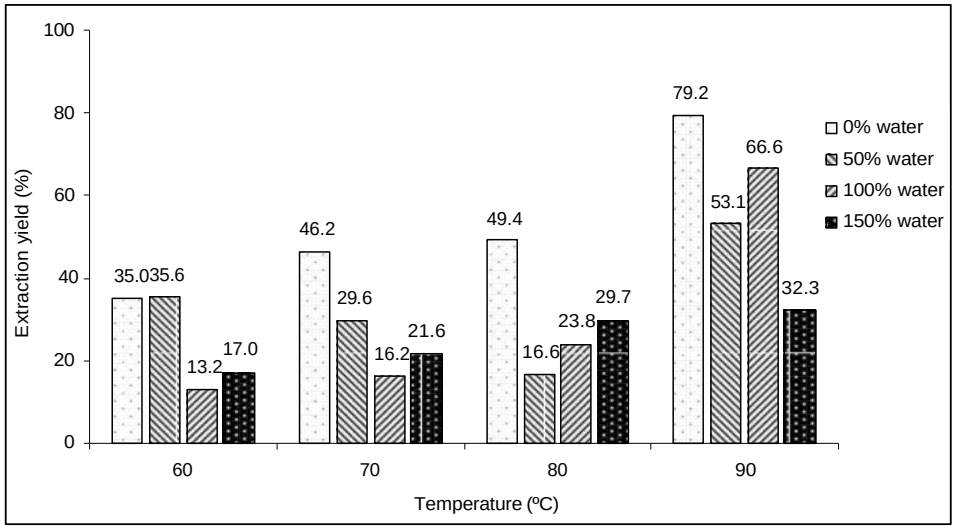

Figure 2. Fat extraction yield *versus* amount of water and temperature (6 hours, without enzyme).

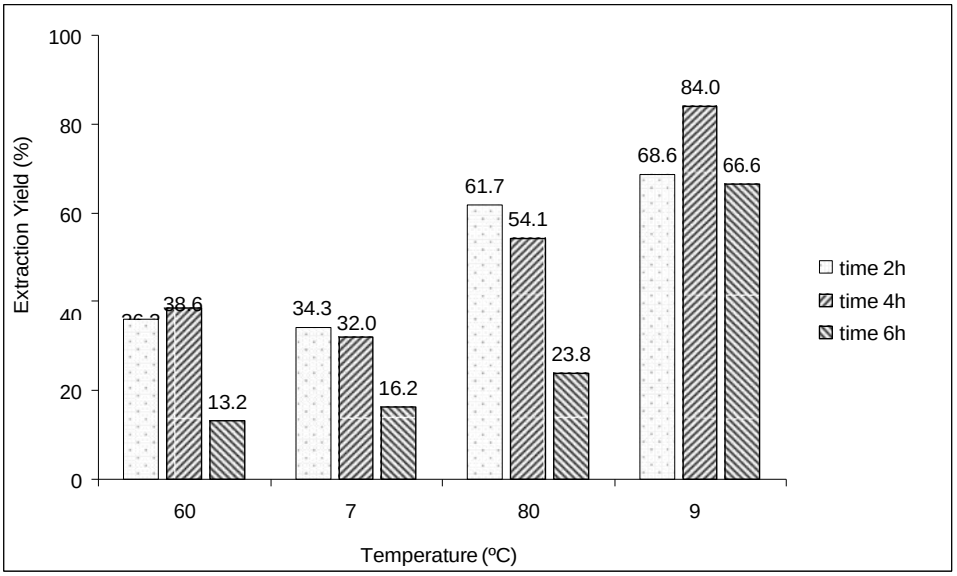

Figure 3. Fat extraction yield *versus* contact time and temperature (100% of water without enzyme).

TABLE XI
Fat used in oils production characterization

Parameter	Results
Acid value (mg KOH/g fat)	2.5
Iodine value (g iodine/100g fat)	43.7
Saponification value (mg KOH/g fat)	175.0

3.3 Hydrolysate treatment

The results from protein hydrolysate characterization are shown in Table XIII.

3.4 Leather treatment and evaluation

The oils and hydrolysate products were used for leather retanning, dyeing and fatliquoring according to

TABLE XII
Oils produced characterization

Oils	S1	S2	S3	S4
Combined SO_3 (%)	0.7	1.2	2.3	3.4
Acid value (mg KOH/g oil)	8.9	7.9	19.9	22.5
Saponification value (mg KOH/g oil)	87.6	72.1	83.2	99.8
Iodine value (g iodine/100g oil)	25.5	14.1	12.2	11.6

TABLE XIII
Protein hydrolysate characterization

Parameter	Results
Solids content (%)	4.9
Mineral matter (% dry basis)	26.0
Organic matter (% dry basis)	74.0
Kjeldahl nitrogen (mg/L)	9,244.6

TABLE XIV
Results of physical-mechanical tests, 1.8mm thickness leather samples

Trial	Chemical tested	Tear strength (N)	Ball burst test	
			Load	Distension
G	–	162.9	540.5	9.59
G1	Oil S1	126.6	485.0	9.71
G2	Oil S2	128.8	516.5	9.98
G3	Oil S3	115.9	456.3	10.50
G4	Oil S4	214.1	615.2	9.31
G5	HP	244.6	728.7	8.70
G6	HP	224.6	642.0	8.82
G7	GHP50	211.0	568.5	8.79
G8	GHP100	191.5	518.0	8.64

TABLE XV
Results of physical-mechanical tests, 1.2mm thickness leather samples

Trial	Chemical tested	Tear strength (N)	Ball burst test	
			Load	Distension
T	–	58.0	336.3	9.25
T1	Oil S1	112.6	433.8	9.98
T2	Oil S2	77.5	374.2	10.47
T3	Oil S3	87.4	388.7	10.60
T4	Oil S4	50.6	285.7	10.00
T5	HP	86.2	541.3	10.70
T6	HP	41.6	256.5	9.20
T7	GHP11	54.2	289.5	9.60
T8	GHP34	66.1	337.4	9.70
T9	GHP50	76.5	291.6	8.50
T10	GHP100	120.1	460.8	9.70

data in Tables IV and V using about 80g of shaved wet-blue bovine leather (two pieces of leather). The obtained leather samples were then dried, staked and submitted to physical and mechanical tests – two samples for each trial. The results obtained were compared with the results of the standard using processes, T and G, using the reference values for footwear application: 200N for load and 7mm for distension in ball burst test; 120N and 50N in tear strength respectively for 1.8mm and 1.2mm thickness leather samples. The results are shown in Tables XIV and XV.

The results for the leather with thickness of 1.8mm (Table XIV) are very good compared with the reference values, except for the tear strength of trial G3. The evaluation of the leather pieces showed a good softness and grain firmness.

The results for the thickness of 1.2mm (Table XV) are also very good when compared with the reference values, with the exception of trial T6. The evaluation of the leather pieces obtained showed a good softness and grain firmness.

Although the tear strength result of two trials is not good, the overall results show good potential for the developed products. Tests at a bigger scale, using entire hides, will be used to provide the technical validation of these laboratory results.

4. CONCLUSIONS

The present work has shown the possibility of adding value to tannery fleshings for the production of oils and hydrolysate products which can be used in the processing of hides and skins, namely in fatliquoring and retannage processes.

Fat extraction from the fleshings is better when enzyme or a high temperature is used. Thus, a maximum extraction yield of 93% is obtained for the hydrolysis conditions: 60°C, 4 hours, 2% of enzyme and 100% of water.

Leather samples, obtained using sulphated oils and hydrolysate products, were evaluated through physical-mechanical tests and presented very good results, always above the reference values for footwear application. It was found that leather samples obtained showed good softness and grain firmness.

The valorization of this waste results in a double advantage for the leather industry: it reduces the environmental impact of the leather industry and allows the production of agents that are an alternative to some chemicals used in the fatliquoring and retannage of leather. A validation of these results at a larger scale will be important.

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