LIFE GOAST GREEN ORGANIC AGENTS FOR SUSTAINABLE TANNERIES (LIFE16 ENV/IT/000416)

R. Pasquale[1], C. Bortolati[1a], F. Serafini[1], M. Signoretto[3], S. Tieuli[3], M. Silvestri[2], L. Frighetto,[2] L. Culpo[4], E. Mistrorigo[4], E. Pivetti[4]

1 GSC GROUP SPA, Montebello Vic.no, Italy, 2 PASUBIO SPA, Arzignano, Italy, 3 Università Ca' Foscari- Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Venezia, Italy, 4 MEDIO CHIAMPO S.P.A., Montebello Vic.no, Italy; a) Corresponding author: claudiobortolati@gscspa.it .

Abstract. LIFE GOAST Green Organic Agents for Sustainable Tanneries (LIFE ENV/IT/000416) belongs to European LIFE programme which supports and promotes the research and innovation on environmental and sustainability topics. The project started on July 2017 and is an ongoing investigation, and involves the competences of three direct actors in the leather industry such as GSC Group spa as chemical supplier, Conceria Pasubio as tannery and Mediochiampo as waste-water treatment agency, in conjunction with the expertise of Università 'Ca Foscari di Venezia. It aims at demonstrating the benefits of a new tanning technology on a semi-industrial scale, particularly focusing at the tanning stage of the leather manufacture, and put itself as a more sustainable alternative to Traditional Chrome Tanning Process (TCTP). The technical feasibility of LIFE GOAST implementation, as well as its social and economic impact, have been monitored and compared with the TCTP in order to demonstrate the reduced environmental impacts of the new process, while producing comparable or better quality leather. It was then demonstrated that it was possible to treat collagen with the GOAST technology to give stabilised collagen to be used in the leather industry. A series of leather swatches were realised according to the new protocol in order to obtain preliminary information on chemical oxygen demand COD of the effluents and technical feasibility of the process. The results were remarkable: the collected waste-water generated from tanning and retanning showed COD values in line with TCTP and it was possible to obtain soft and firm grain leather despite a shrinkage temperature lower than chromium process.

Keywords: Clean technology, water quality, hazardous substance, tanning, sustainability.

1 Introduction

Leather manufacturing is classified as water, energy and waste intensive by the Industrial Emissions Directive (2010/75/EU); it requires the combination of different physical and mechanical actions and the utilisation of various chemical substances, which range from simple inorganic salts to more complex organic substances and polymers. As a consequence, both such elements and tannery effluents generated, could cause significant damage to soil and water bodies, and therefore could lead to safety and environmental concerns, if not properly used and/or treated respectively.

The European IPPC Bureau report 2013 states that at present over 85 % (w/w) of the world leather production is chrome tanned and only a minor part is manufactured with alternative processes. Worldwide, shoe leathers (uppers and linings) are the dominant leather types, although upholstery leather, especially automotive leather, is winning an increasing market share (see the Distretto Vicentino della Pelle in the Arzignano area of Veneto, Italy). An estimated 7×10^6 t of hides and skins containing about 2.8×10^6 t of collagen are used yearly worldwide for leather production, although, unfortunately, due to technical reasons only 50 % of the hide collagen is converted into leather (Buljan, Reich, & Ludvík, 1998). The loss of water by samming, loss of collagen due the shaving processes influence the overall low yield of the leather manufacture; the focus of the tanning is clearly to stabilise and preserve the collagen, but also to reduce the thickness of the leather article, which is in relationship with the remarkable mass loss. (Reich, Die Nutzung von Kollagen außerhalb der Lederindustrie, Teil I: Allgemeines und Einsatzgebiete mit hoher, 1995).Therefore, there is an important waste of material which needs to be recovered within the process.

Furthermore, the current use of chrome poses serious environmental and health problems due to the potential formation of carcinogenic Cr (VI) in finished articles, prompting users to find innovative solutions. Table 1 summarises the chemicals and water balance required for the production of approximately 1000 m^2 of chrome-tanned shoe upper leather, (Buljan, Reich, & Ludvík, 1998) whilst Table 2 provides the quantities of the most important chemicals (as general class) used for the leather production per annum. (Taeger, 2003) Table 1 is a dated insight and could not perfectly fit with the present parameters, especially with respect to the inorganic and organic acids and the sodium sulphide quantities, which should be increased to 60 and 275 kg respectively. It is noteworthy that the most used chemicals in the leather tanning are water, chromium salts and inorganic salts, and therefore their utilisation should be revised and/or improved in order to give a more sustainable industrial process.

LIFE GOAST implementation aims:

1. to produce *free of chrome* (FOC) high quality leather articles achieved by unprecedented pilot scale implementation of LIFE GOAST.
2. to improve the quality of tannery effluents by total reduction of chromium salts, acids/bases sodium chloride in tanning and retanning steps, since no chrome, nor pickling (acid treatment) or basification, typically foreseen when chromium is used;
3. to demonstrate lower environmental impact of LIFE GOAST technology in terms of reduction of hazardous substances, environmental risks (human and ecological), primary resource consumption (water) due to simplification/reduction of industrial steps to process hides, according with the 7th Environment Action Programme, and environmental releases in water and soil;
4. to eliminate/reduce the chrome containing sludge.

The project started on July 2017 and is an ongoing investigation: at present, the entire team is working with respect of the optimisation of the leather production through the LIFE GOAST technology and the re-utilisation/recycle of the aqueous waste generated throughout the consequently tanning and retanning steps. Herein, it will be summarized and described the achievements obtained during the implementation.

Table 1. Approximate demand for water and chemicals to produce 1000 m^2 of chrome-tanned grain leather (ca. 7.1 t of wet salted hide) and as by-product 430 m^2 of split leather from cattle hide

Substance	Quantity (kg unless otherwise stated)
Water	215.000
Inorganic salts (NaCl)	570
Inorganic and organic acids	30
Sodium sulphide	175
Calcium hydroxide	285
Enzymes	20
Bactericides	20
Tensides	20
Chrome extracts (Cr_2O_3)	700 (175)
Vegetable tannins	50
Synthetic tannins	50
Polymers	50
Resins	10
Fatliquors	150
Dyestuffs	35
Polymer binders (finishing)	30

Table 2. Quantities of the most important leather chemicals used for world leather production in 2000.

Substance	**Quantity, 10^3 t/y (unless otherwise stated)**
Water	320 x 10^6 m^3
Tensides	120
Lime hydrate	300
Sodium sulphide	200
Sodium chloride	270
Chrome extracts (Cr_2O_3)	1.600
Vegetable tannins	300
Aromatic syntans	150
Glutaraldehyde	30
Resins	30
Polymers	150
Lubricating agents	400
Dyestuffs	90
Polymer binder	200

2 Materials and Methods

The leather auxiliaries involved in the project implementation were provided and produced by *GSC Group spa* and used either at *GSC Group spa* or *Conceria Pasubio* facilities.

The leather used for the trials and the entire project implementation was purchased from *Conceria Pasubio* and used either by *GSC Groups spa* or *Conceria Pasubio* at their facilities.

Leather tests were carried out by *Conceria Pasubio*; thickness measurements were carried according to ISO 2589 using IG/MS (CD-6'') from *Giuliani Tecnologie*. Tear strength (traction), elongation at break of leather (%), elongation at specified load (100 N) were performed according to ISO 3376 using a dynamometer LR 5K from *Lloyd Instrument*. Single edge tear was carried out according to ISO 3377-1 using the previous described dynamometer. Leather softness was performed following ISO 17235 with a softness tester /ST300D from *MSA Engineering*. Gravimetric fogging was carried out according to ISO 17071 with a PC201-FTS (heating) combined with ACCEL250 (cooling) system form *Thermo Scientific.* Reflectrometric fogging was carried out with the same devices, although the measurement was performed with a glossmeter MICROTRIGLOSS from *BYK*. Heat resistance was performed in a heating over FD115 from *Binder.*

Soluble chemical oxygen demand (COD) was monitored and assessed to obtain information on the fixation grade of the chemicals applied in the tanning and retanning tests. COD was determined by LCK 014 and LCK 914 kit analysis in combination with HT 200S as digesting system and DR3800 as spectrometer from *Hach Lange*. The COD values were calculated after filtration of the aqueous solution using filtering paper grade *IF5H*.

Shrinkage temperature was assessed either *via* SHRINKAGE TG TESTER by *Giuliani*.
Analytical gas chromatography for VDA 277 was performed on a GC7820A instrument from *Agilent Technologies* with a FID detector using a DB-WAX UI capillary column (30 m x 0.25 mm i.d.) and helium as carrier gas. Static headspace analyses were carried out using a 7687 headspace sampler from *Agilent Technologies.* Alternatively, analytical gas chromatography was performed on a CLARUS 580 instrument from Perkin Elmer with a SQ8 S detector (EI) using an ELITE-624 MS capillary column (30 mt x 0.25 mm i.d.) and hydrogen as carrier gas. Static headspace analyses were carried out using a TURBOMATRIX HS 40 TRAP from Perkin Elmer, using hydrogen as carrier gas.

Leather shavings were analysed by *Università 'Ca Foscari di Venezia* within the LIFE GOAST implementation and were generated after the leather tanning of at least one entire bovine hide.

Waste-water was analysed by *Medio Chiampo* and *Università 'Ca Foscari di Venezia* in the event of leather tanning and retanning of at least one entire bovine hide.

Metals screening was carried out using MP-AES 4210 by *Agilent Technologies* after microwave-assisted dissolution of waste-water samples by CEM *Discover SP-D*. In the digestion procedure, 2 mL of each samples were mixed with 4 mL concentrated nitric acid and 1 mL oxygen peroxide in the system specific quartz reactor. The digestion lasted for a total of 15 min at 170°C under stirring. After cooling the sample solutions were transferred to 25 mL flask and diluted with *Milli-Q water*. Then, the metals analysis was performed on the samples diluted to 100 times. The viewing position and nebulizer flow for the MP-AES were optimized before each run. The selected elements and the corresponding wavelengths are given in ***Table 3***.

Table 3. Elements and the corresponding wavelengths.

Element	Wavelengths (nm)
Ag	328.068
Al	396.152
Cd	228.802
Co	345.351
Cr	425.433
Cu	324.754
Fe	371.993
Mn	403.076
Ni	361.939
Pb	405.781
Tl	535.046

3 Results and Discussion

3.1 Production of the tanning agents

The tanning agents were developed and produced by the R&D of GSC Group spa and are based on polymeric functionalised acrylic polymers in combinations with synthetic tannins, and are part of an unprecedent research. LIFE GOAST tanning agents belong to acrylic polymers category that could be obtained either via aqueous and/or in-solvent radical polymerization of the appropriate allyl, acrylic, vinyl, methacrylic monomers. Furthermore, chemical functionalization of these species improved the polymer interaction with the collagen in a covalent fashion, to produce a pelt with remarkable physical and chemical properties. An appropriate laboratory protocol for the production was elaborated, and consistent results within the trials were obtained. The scaling-up process from lab-scale to semi-industrial scale is currently in progress; despite our implementation produced different species of polymers, it was decided to focus on a single version of the polymer, since it produced remarkable results in terms of tanning properties. So, this summary will concentrate on the utilisation of the **GOAST TANNING AGENT 8555/1**, which was produced and characterised between 2017-18; the tanning agent is a white dispersion of resin in water with 50% dry residue and approximately pH 4.00.

3.2 Production and characterization of leather articles

Before the actual tannage, the hides and skins were prepared following the standard procedure for the TCTP. LIFE GOAST technology aims at substitute the chrome tannage, and therefore it inserts perfectly within the standard procedure. The LIFE GOAST tanning protocols consist on a series of mechanical and chemical actions performed on the raw hide to give tanned leather (see ***Table 4***, ***Table 5***, ***Table 6*** and ***Table 7*** as examples).

The mechanical action performed consisted in rotation of the tanning drum and the heating of the vessel, whilst, the chemical actions consisted of the addition of the chemicals (tanning agents), pH adjustment via addition of bases (sodium bicarbonate) or weak acids (formic acids).

After the tanning step, the hides were sammed to get rid of the excess of water and shaved, followed by retannage. It is important to underline that the leather shavings constitute an important by-product of the tannage process, and also of the LIFE GOAST technology; however, our team is currently investigating at the revaluation of the shavings to give novel and less environmental impacting products (see 3.4). Finally, the hides were retanned with a specially developed procedure. Herein, specifications and data related to several experiments carried out during the investigation are reported; the given examples focus on car-interior leather production. ***Table 4***, ***Table 5*** and ***Table 6*** depict typical procedures for the LIFE GOAST tanning technology; water is still unfortunately the most abundant chemical used in the process, as it is found in TCTP, although preliminary calculations showed that water is slightly less impacting for LIFE GOAST than in TCTP (this investigation is still in progress) Such examples led to a white-brownish leather which exhibited a shrinkage temperature between 70°C to 75°C right after the tannage; the tanning floats showed COD between 20000 mg O_2/l to 60000 mg O_2/l, depending on the combination of tanning and the GOAST TANNING AGENT 8555/1 concentration. It is important to underline that the processed hides were easily shaved to 1.0 to 1.2 mm thickness, to get the intermediate to be retanned as reported in ***Table 7***.

Table 4. LIFE GOAST tanning procedure example #1

Articolo/*Article*:			LIFE GOAST TANNING EXAMPLE 1			
Tipo pelle/*Type of Leather*:	Bovine Hide			Spessore/*Thyckness*:		
				Peso/*Weight* [g]:		20.000
Operatore/*Operator*:						
%	**Prodotti** ***Products***	**Quantità** ***Q.ty*** **[g]**	**Temp. [°C]**	**Tempo** ***Time***	**pH**	**Operazione** ***Operation***
100,00%	WATER		30°C			
9,00%	NaCl			20'		**6/7 Bè**
2,50%	GOAST TANNING AGENT 8555/1			120'		
6,00%	SYNTAN 01					
12,00%	SYNTAN 02			180'	**3**	
0,20%	SODIUM BICARBONATE			30'		
0,20%	SODIUM BICARBONATE			30'		
0,20%	SODIUM BICARBONATE			30'		
0,10%	SODIUM BICARBONATE			30'	**4**	
						SLOW, AUTOMATIC
	DAY AFTER				**3.8**	**DRAIN WASH**
150,00%	WATER		20°C			
0,50%	OXALIC ACID			30'		**SCARICARE**
NOTE						

The application and the use of the products are beyond our control and they shall be exclusively on the customer's responsability.

Table 5. LIFE GOAST tanning procedure example #2

Articolo/*Article*:			**LIFE GOAST TANNING EXAMPLE 2**			
Tipo pelle/*Type of Leather*:	Bovine Hide		Spessore/*Thyckness*:			
			Peso/*Weight* [g]:			20.000
Operatore/*Operator*:						
%	**Prodotti** ***Products***	**Quantità** ***Q.ty*** **[g]**	**Temp. [°C]**	**Tempo** ***Time***	**pH**	**Operazione** ***Operation***
100,00%	WATER		30°C			
9,00%	NaCl			20'		**6/7 Bè**
3,25%	GOAST TANNING AGENT 8555/1			120'		
7,00%	SYNTAN 01					
10,00%	SYNTAN 02				**3**	
1,00%	SYNTAN 03			180'		
0,20%	SODIUM BICARBONATE			30'		
0,20%	SODIUM BICARBONATE			30'		
0,10%	SODIUM BICARBONATE			30'	**4**	
						SLOW, AUTOMATIC
	DAY AFTER				**3.8**	**DRAIN WASH**
150,00%	WATER		20°C			
0,50%	OXALIC ACID			30'		**SCARICARE**
NOTE						

The application and the use of the products are beyond our control and they shall be exclusively on the customer's responsability.

Table 6. LIFE GOAST tanning procedure example #3

Articolo/*Article*:			**LIFE GOAST TANNING EXAMPLE 3**			
Tipo pelle/*Type of Leather*:	Bovine Hide		Spessore/*Thyckness*:			
			Peso/*Weight* [g]:			20.000
Operatore/*Operator*:						
%	**Prodotti** ***Products***	**Quantità** ***Q.ty*** **[g]**	**Temp. [°C]**	**Tempo** ***Time***	**pH**	**Operazione** ***Operation***
100,00%	WATER		30°C			
9,00%	NaCl			20'		**6/7 Bè**
5,00%	GOAST TANNING AGENT 8555/1			120'		
9,00%	SYNTAN 01					
9,00%	SYNTAN 02			180'	**3**	
0,20%	SODIUM BICARBONATE			30'		
0,20%	SODIUM BICARBONATE			30'		
0,10%	SODIUM BICARBONATE			30'	**4**	
						SLOW, AUTOMATIC
	DAY AFTER				**3.8**	**DRAIN WASH**

150,00%	WATER		20°C			
0.50%	OXALIC ACID			30'		**SCARICARE**
NOTE						

The application and the use of the products are beyond our control and they shall be exclusively on the customer's responsability.

Table 7. LIFE GOAST retanning procedure car interior example #1

Articolo/*Article*:		**CAR INTERIOR 1**				
Tipo pelle/*Type of Leather*:		Tanned Bovide Hide from LIFE GOAST		Spessore/*Thyckness*:		1,1/1,2
				Peso/*Weight* [g]:		7.000
	Operatore/*Operator*:					
%	**Prodotti** ***Products***	**Quantità** ***Q.ty*** **[g]**	**Temp. [°C]**	**Tempo** ***Time***	**pH**	**Operazione** ***Operation***
200,00%	WATER	14.000	30°C			
0,50%	OXALIC ACID	35,0				
0,50%	SURFACTAN 1	35,0		60'		DRAIN WASH
		0,0				
100,00%	WATER	7.000	30°C			
1,00%	SODIUM ACETATE	70,0		60'	**4**	DRAIN WASH
		0,0				
100,00%	WATER	7.000	30°C			
1,00%	FATLIQUOR 1	70,0				
3,00%	FATLIQUOR 2	210.0		60'		
16,00%	SYNTAN 1	1.120,0				
6,00%	VEGETABLE TANNIN 1	420,0				
6,00%	SYNTAN 2	420,0		30'		
2,00%	FATLIQUOR 1	140,0		10'		
16,00%	SYNTAN 1	1,120.0				
7,00%	VEGETABLE TANNIN 1	490,0		90'		**SLOW, OVERNIGHT**
	DAY AFTER	0.0				
200,00%	WATER	14.000,0	50°C			
1,00%	FORMIC ACID	70,0		10'		
1,50%	FORMIC ACID	105,0		30'		**COD 41900 mg O2/l**
		0.0				DRAIN
150,00%	WATER	10.500,0	50°C			
5,00%	FATLIQUOR 2	350,0				
4,00%	FATLIQUOR 1	280.0		60'		
1,00%	FORMIC ACID	70.0		10'		
0,50%	Al2(SO4)3	35.0		60'		**COD 28000 mg O2/l**
		0.0				DRAIN
150.00%	WATER	10,500.0	50°C			DRAIN

			0.0						
200,00%	WATER		14.000,0	20°C	10'		DRAIN		
200,00%	WATER		14.000,0	20°C					
0,30%	OXALIC ACID		21,0						
NOTE	**VACUUM 40°**								
The application and the use of the products are beyond our control and they shall be exclusively on the customer's responsability.									

It is then summarised a series of analyses and test-results for the characterisation of the retanned LIFE GOAST leather obtained with these specially designed protocols, which finalise the achievements accomplished throughout the implementation. The results are yet not fully satisfactory, and do not entirely meet the requirements in order to be correctly processed as car-interior leather (red), although they are still promising (see ***Table 8***). It is necessary to underline that these results are referred to the GOAST TANNING-42 which is based on the tanning and retanning procedures reported in ***Table 6*** and ***Table 7*** respectively, and potential improvements are hypothesised for the entire process. Difficulties in the delivery of the functionalised polymer were experienced, although with modification at the addition rates and pH they were overcame. The final results were still satisfactory and prompted our investigation for the future leather tanning tests.

Table 8. Summary of the physical and chemical tests run on LIFE GOAST leather.

TEST	METODO	REQUIRED	FOUND
Thickness	ISO 2589	1,2-1,5	1,36 mm
Tear strength (traction)t	ISO 3376	≥130 N (average 3 values)	L=178,15 T=169,00
Elongation at break of leather (%)	ISO 3376	30-70% (average 3 values))	L=45,8 T=34,04
Softness (ST 300)	ISO 17235	3,5-4,5 mm	3,6 mm
Elongation at a specified load (100N)	ISO 3376	8-25% (average 3 values)	L=31,45 T=23,97
Single edge tear	ISO 3377-1	≥25 N average 3 values)	L=16 T=16,37
Gravimetric fogging	ISO 17071	≤ 3,00 mg	2,01 mg
Reflectrometric fogging	SAE J1756	≥ 70%	68,25
Heat resistance	(48±1h;80±2°C)	≥ 4 GS	OK
VDA 277		< 100 ppm	76ppm

3.3 Waste-water Analysis from the LIFE GOAST process

Waste water generated through the tanning and retanning implementation were carried out; basic COD and metal content analyses were monitored (see 3.2).

Zahn-Wellens tests were carried out with the waste-water generated from the LIFE GOAST tanning process; this methodology is used to evaluate the potential biodegradability of water-soluble and non-volatile organic substances exposed to relatively high concentrations of microorganisms at static conditions. Furthermore, this study will allow to asses the pattern of use and degradation of carbon within 28 days under controlled pH, temperature and dissolved oxygen conditions by the active biomass coming from the biological reactors in our purification plant. This study is still under investigation, although preliminary results are herein described.

Preliminary investigation on waste-water generated from the tanning and retanning showed that biological degradation stopped at about 70%, thus meaning that an approximately 30% of the soluble carbon is not biodegradable within 28 days (*Fig. 1*). The result was found to be reproducible with two different set of experiments, which were carried out at the beginning of 2018; unfortunately, the results did not show complete degradation, possibly due to non-ideal conditions of degradation (choice of microorganism pool). However, the residual from the biological degradation was found still found to be organic, which led the hypothesis of an easier treatment *via* precipitation, sludge formation and thermal degradation without harmful by-products.

Table 9 reports the content for metal analysis carried out on a tanning and retanning experiment, named **GOAST TANNING-54**; this experiment used the procedure reported in ***Table 6*** followed by the application of retanning from ***Table 7***. Each entry in the first bold column identifies a portion of the generated waste water, which were isolated for the determination; prefixes T and R stands for *tanning* and *retanning* respectively, whilst suffix S stands for SURNATANT. The results of metals analysis showed a low to a negligible amount of metals in the LIFE GOAST tanning liquor. The traces of chrome observed in the tanning water waste could be ascribed to a previously contamination of both tannery drum and used water. In addition to this, general parameters for water analysis were monitored (see ***Table 10***). More efficient waste-water treatment is therefore required and is still under investigation.

Table 9. Results of metals analysis of the GOAST-TANNING-54

	Cd (ppm)	Ag (ppm)	Cu (ppb)	Co (ppm)	Pb (ppb)	Mn (ppm)	Cr (ppm)	Tl (ppm)	Ni (ppm)	Fe (ppm)	Al (ppm)
T-T54	n.d	<20 ppb	n.d	n.d	n.d	<20 ppb	4,3	n.d	n.d	-	2,1
T-sT54	n.d	<20 ppb	n.d	n.d	n.d	<20 ppb	4,5	n.d	n.d	-	2,1
R-T54	n.d	2,1	n.d	n.d	n.d	<20 ppb	3,9	n.d	3,7	-	<20 ppb
R-sT54	n.d	2,3	n.d	n.d	n.d	<20 ppb	2,8	n.d	5,3	-	<20 ppb
F-T54	n.d	<20 ppb	n.d	n.d	n.d	<20 ppb	<20 ppb	n.d	1,7	-	6,5
F-sT54	n.d	<20 ppb	n.d	n.d	n.d	<20 ppb	<20 ppb	n.d	2,4	-	6,0

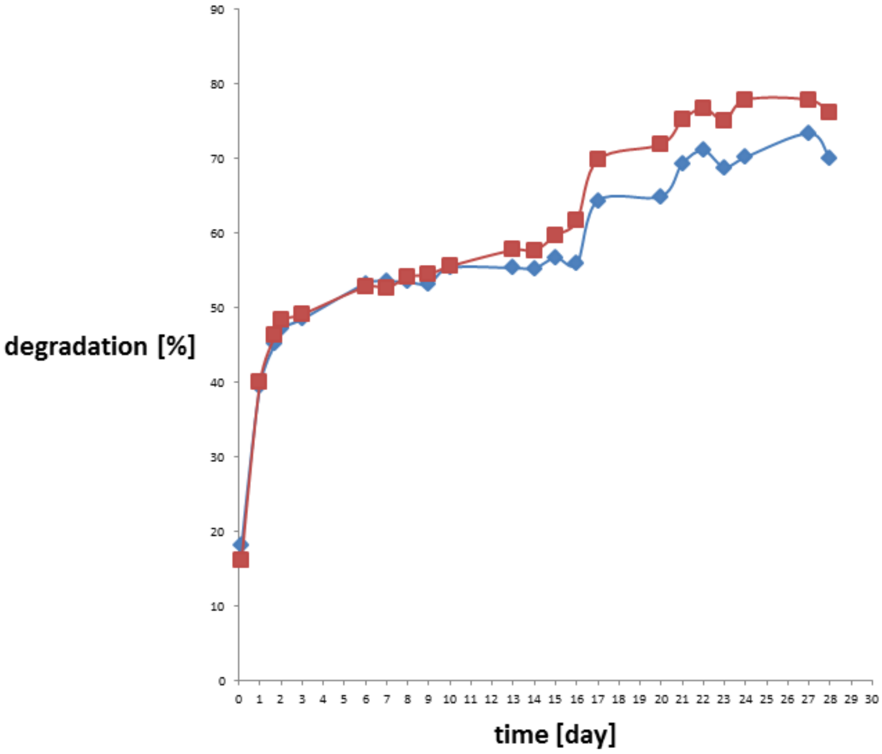

Fig. 1. Biological degradation of two sets of waste water generated from the LIFE GOAST tanning according to Zahn-Wellens tests

Table 10. Water parameters for LIFE GOAST effluent obtained from preliminary study.

Parameter	Waste-water
TKN (mg N/l)	571
COD (mg O2/l)	44000
DOC (mg C/l)	14340
pH	6.28
Ammonia (mg NH4/l)	384
Tn (mg N/l)	441
Chlorides (mg/l)	16574
Sulphates (mg/l)	4101
Nitrates (mg/l)	N.D.
Conductivity (μS/cm)	61000

3.4 Revaluation of the Shavings from the LIFE GOAST Process

Tanning hide into leather is a very complex process, which has a large number of steps and generates substantial quantities of solid and liquid wastes. As reported by Sundar *et al.* (Sundar, Gnanamani, Muralidharan, Chandrababu, & Mandal, 2011) processing of 1000 kg of rawhide produces on an average 200 kg of tanned leather, 450 kg of solid wastes and 50,000 kg of waste water. Therefore, due to this high environmental impact many efforts have been made in recent decades for the treatment of solid wastes from the pre-tanning, tanning and post-tanning processes in the leather industry (Jiang , Liu, & Han , 2016). In this context, pyrolysis could be considered one of the possible approaches for the treatment of solid wastes from the tanning industry.

Leather solid wastes produced by GOAST technology have the advantage of being Cr-free, which can be easier recyclable than chromium-tanned solid wastes. In view of this, an effective and sustainable process for the valorisation of leather waste produced by GOAST technology is under investigation by Ca'Foscari University. The attention was focused on the enhancement of GOAST shaving waste for the production of "biochar" by pyrolysis and its application as soil improver or fertilizer (Yang , et al., 2016, p. 36:36), (Cha, et al., 2016). This project aims at avaluating the best pyrolysis conditions with the purpose to achieve the right compromise between bio-oil yield and bio-char yield, and to obtain a bio-char with best characteristics and agronomic properties for "soil improver" application. The optimal pyrolysis conditions have been investigated taking into account the effect of different parameters, such as temperature, heating rates, time, grinding size of raw material and inert flow rate, on the characteristics of biochar. In ***Fig. 2*** it is shown the distribution of the generated fractions (char, condensable and gas fraction) obtained in function of grinding size. The best pyrolysis conditions were found to be 600°C temperature, heating rate 10°C/min, hold temperature for 30 minutes; this process was carried out at 100 mL/min of nitrogen for the laboratory testing.

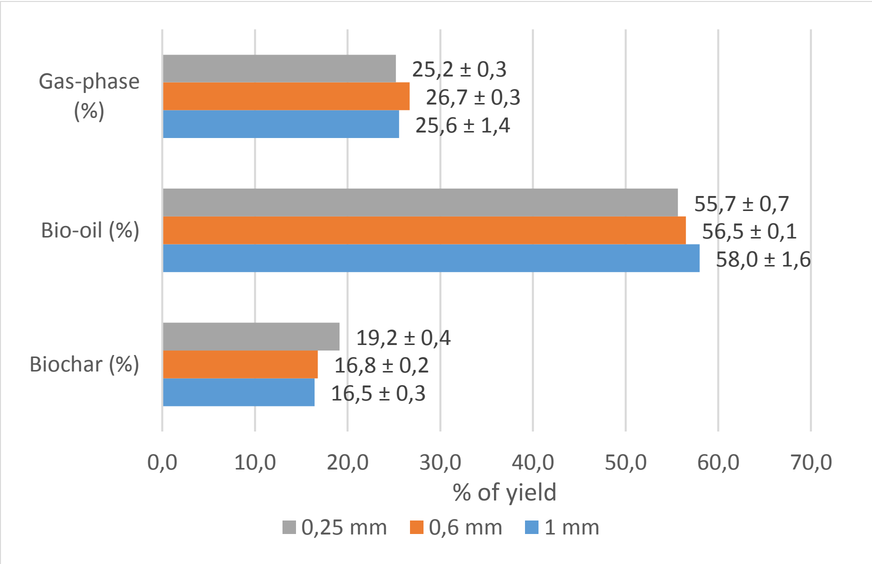

Fig. 2. Yield (%) of the generated fractions (char, condensable and gas fraction) vs grinding size (mm).

4 Conclusions

This investigation showed that LIFE GOAST technology could be used as an alternative to TCTP; despite the results achieved are not entirely satisfactory, LIFE GOAST produces leather is still promising and could lead to a less impacting tanning technology in the near future. LIFE GOAST leather showed a firm grain surface, sufficient softness and low emission (both VOC and medium volatile compounds).

The reported LIFE GOAST procedures for both tanning and retanning (***Table 4***,***Table 5***, ***Table 6*** and ***Table 7***) are only examples obtained from the implementation and should not be set as the conclusive guidelines for our investigation. It is expected that by the end of the project, the procedure will be updated and improved in terms of shrinkage temperature and COD and leather performances due to the application of specially-designed leather auxiliaries. It is remarkable that, despite the different nature of the chemistry below LIFE GOAST, such technology could be simply applied within the previous procedure for TCTP, substituting the addition of the chrome salts, to give tanned leather. In addition, the leather auxiliary tested for this implementation in terms of fatliquors and retanning agents are simply the same used in the TCTP, which points out that LIFE

GOAST technology is definitely an alternative to TCTP which is based to a different completely organic-tanning system.

It is noteworthy that crust leather obtained by LIFE GOAST technology showed to be more environmental friendly than the TCTP counterpart, due to the absence of heavy metals in the tanning liquor (easier waste-water treatment) and a reduced contribution to the VOC emission. No chromium-salts were involved in the LIFE GOAST trials, and therefore the consequent waste-water, sludge and leather shavings did not contain this element; however, the investigation of the aqueous waste showed traces of chromium and nickel, although it was believed to be a contamination of the floats. Aluminium was found in the floats, sludge and in the leather shavings, which is in line with the contents from one of the retanning strategies of the leather developed in the investigation. Novel chemical auxiliaries for fatliquoring and retanning will be investigated in the future to improve the retanning stege of the process; in fact, it is believed that the utilisation of standard TCTP auxiliaries could not be suitable for the LIFE GOAST process since the basis of the tanning technology are completely different. Despite the satisfactory results accomplished since the beginning of the implementation, it is believed that the design of special auxiliaries will improve the COD of entire leather process and will lower the water demand.

Despite car-interior leather have highly demanding requirements, LIFE GOAST leather seemed to be suitable for this purpose; the implementation is still in progress, but the technology will be suitable for this application, especially in terms of VOC emission and firm leather.

Future work will be carried out on split leather, in order to include different articles and manufactures. In addition, the implementation on the leather shavings revaluation will be highly important for the project.

5 Acknowledgements

The LIFE GOAST team would like to acknowledge the EC for fundings (LIFE16 ENV/IT/000416) and the single partners for the remarkable job carried out since the beginning of the project. Special thanks should be done to *GSC Group spa*, *Conceria Pasubio*, *Medio Chiampo* and *Università 'Ca Foscari di Venezia*.

References

1. *Buljan, Reich, & Ludvík. (1998). Mass Balance in Leather Processing. Leder & Häutemarkt, 4, 30; 5,25.*
2. *Cha, J., Park, S., Jung, S., Ryu, C., Jeon, J., Shin, Park, Y. (2016). Production and Utilization of Biochar: A Review. Journal of Industrial and Engineering Chemistry, 1-15.*
3. *Jiang , H., Liu, J., & Han , W. (2016). The status and developments of leather solid waste treatment: A mini-review. Waste Manag Res,, 399-408.*
4. *Reich. (1995). Die Nutzung von Kollagen außerhalb der Lederindustrie, Teil I: Allgemeines und Einsatzgebiete mit hoher. Leder, 46, 2.*
5. *Sundar, V., Gnanamani, A., Muralidharan, C., Chandrababu, N., & Mandal, A. (2011). Recovery and utilization of proteinous wastes of leather making : a review. Reviews in Environmental Science and Bio/Technology, 151-163.*
6. *Taeger. (2003). Innovative Chemie für einen alten Rohstoff–Erste Schritte auf dem Weg zur nachhaltigen Lederherstellung. Leder & Häute Markt, 9, 33-38.*
7. *Yang , D., Yunguo , L., Shaobo , L., Zhongwu , L., Xiaofei , T., Xixian , H., Bohong , Z. (2016). Biochar to improve soil fertility. A review. Agron. Sustain. Dev., 36.*