Innovative fully biodegradable mulching films & fruit protection bags for sustainable agricultural practices LIFE14 ENV/ES/00048

LIFE MULTIBIOSOL

NEW TANNING AGENTS FROM BIOMASS

Anna Maria Raspolli Galletti[a] and Valerio Talarico[b]

[a] Department of Chemistry and Industrial Chemistry , Via G. Moruzzi 13, 56123 Pisa (Italy), anna.maria.raspolli.galletti@unipi.it

[b]Po.Te.Co., Polo Tecnologico Conciario, via S. Tommaso 119, Santa Croce sull'Arno (Pisa).

General context

Increasing demand of chemicals, energy and fuels

Depletion of easily available petroleum resources

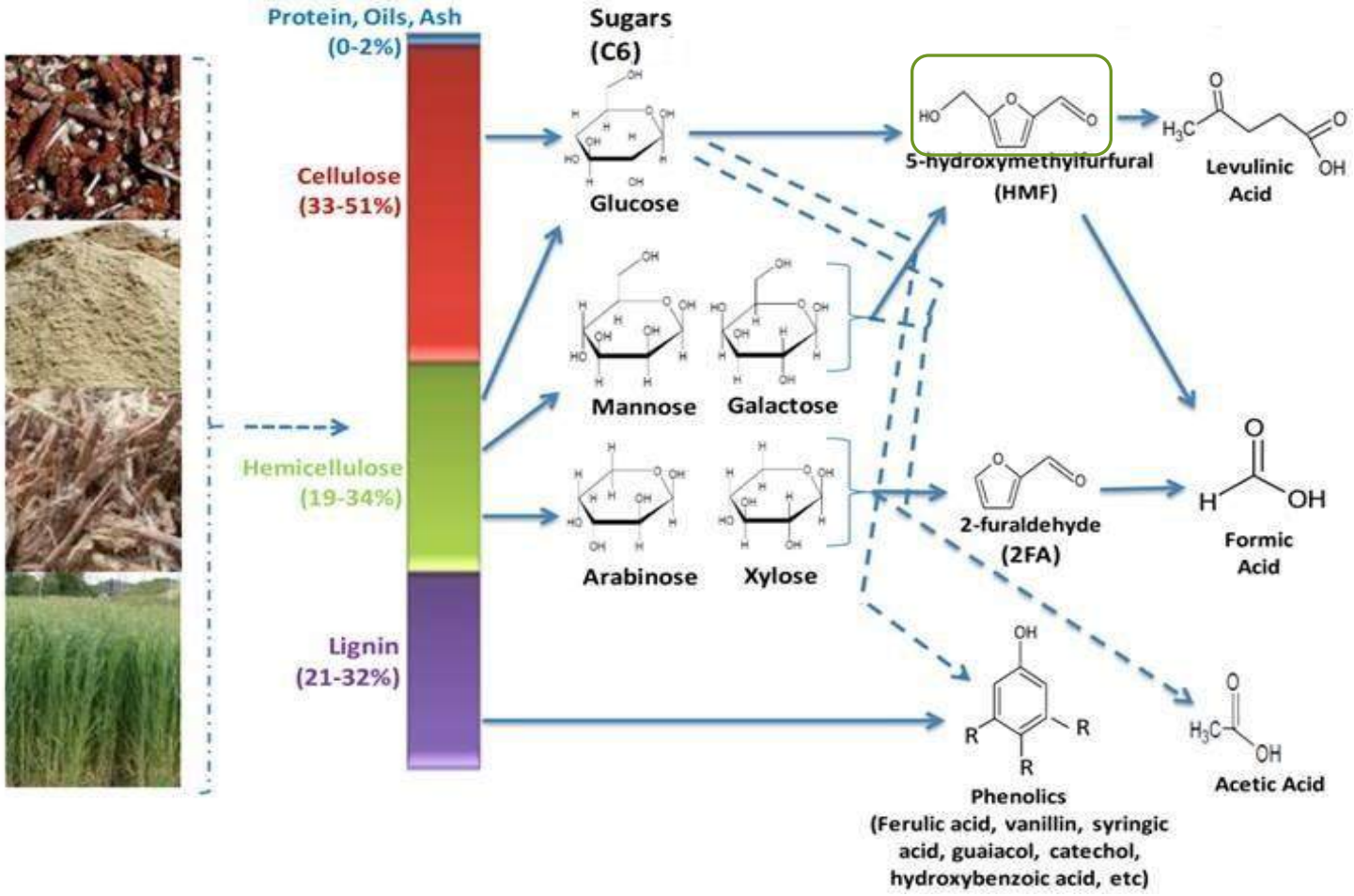
Need of reducing greenhouse gas levels in the atmosphere

Search of alternative energy and new carbon sources

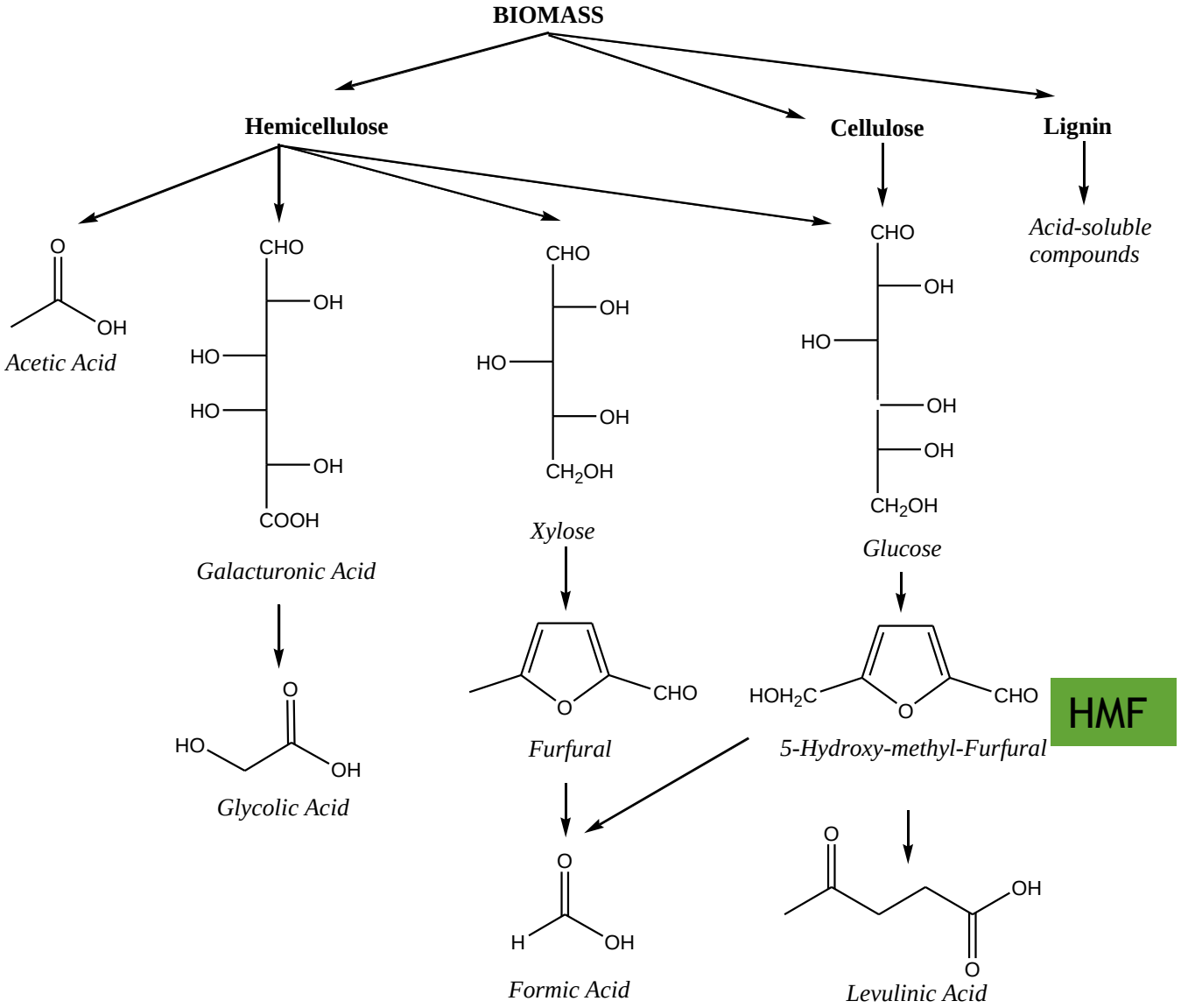
Lignocellulosic biomass is a big source of photosynthetically fixed carbon

The hydrolytic route for the conversion of lignocellulose

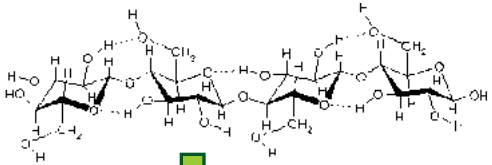
- Lignocellulose can be separated into its components :
- Lignin
- Cellulose
- Hemicellulose
- They are then depolymerized to the corresponding building blocks.
- Mild reaction conditions can be employed.
- A relatively reduced number of products can be obtained with high selectivity.
- Several of them can be employed as raw materials for the synthesis of a variety of compounds with applications as chemicals and/or biofuels.
- The former are considered platform molecules.

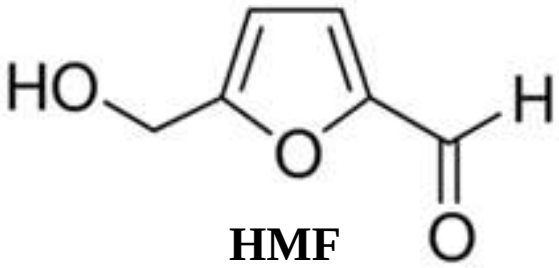

Protein, Oils, Ash
(0-2%)
Cellulose
(33-51%)
Hemicellulose
(19-34%)
Lignin
(21-32%)
Sugars
(C6)
Glucose
Mannose
Galactose
Arabinose
Xylose
5-hydroxymethylfurfural
(HMF)
Levulinic
Acid
2-furaldehyde
(2FA)
Formic
Acid
Acetic Acid
Phenolics
(Ferulic acid, vanillin, syringic
acid, guaiacol, catechol,
hydroxybenzoic acid, etc)

(Auto)hydrolysis of biomass

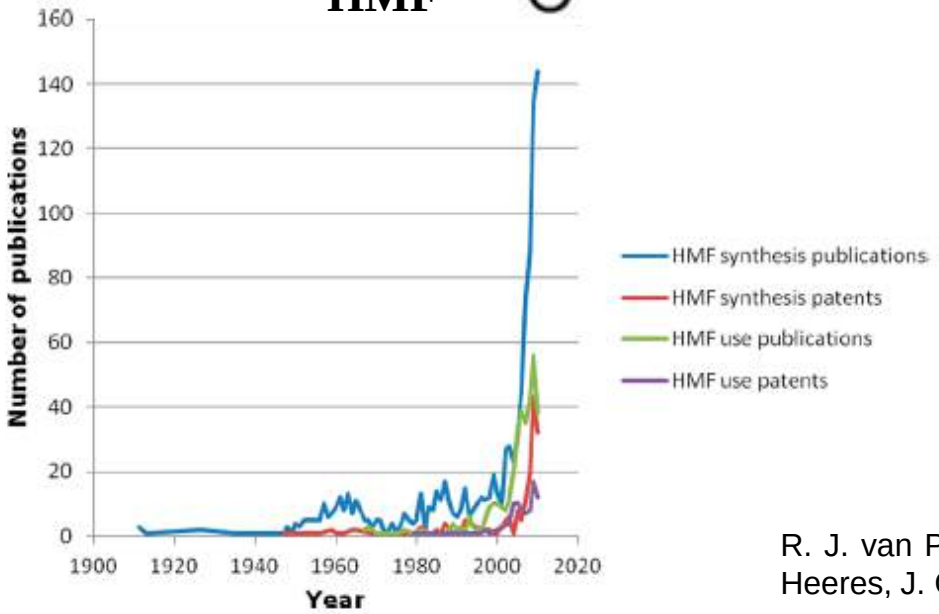


Cellulose

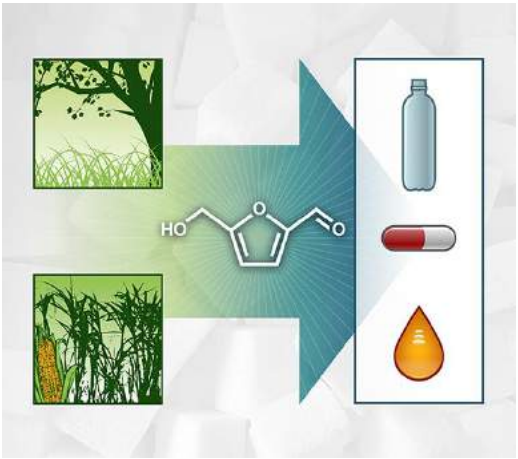




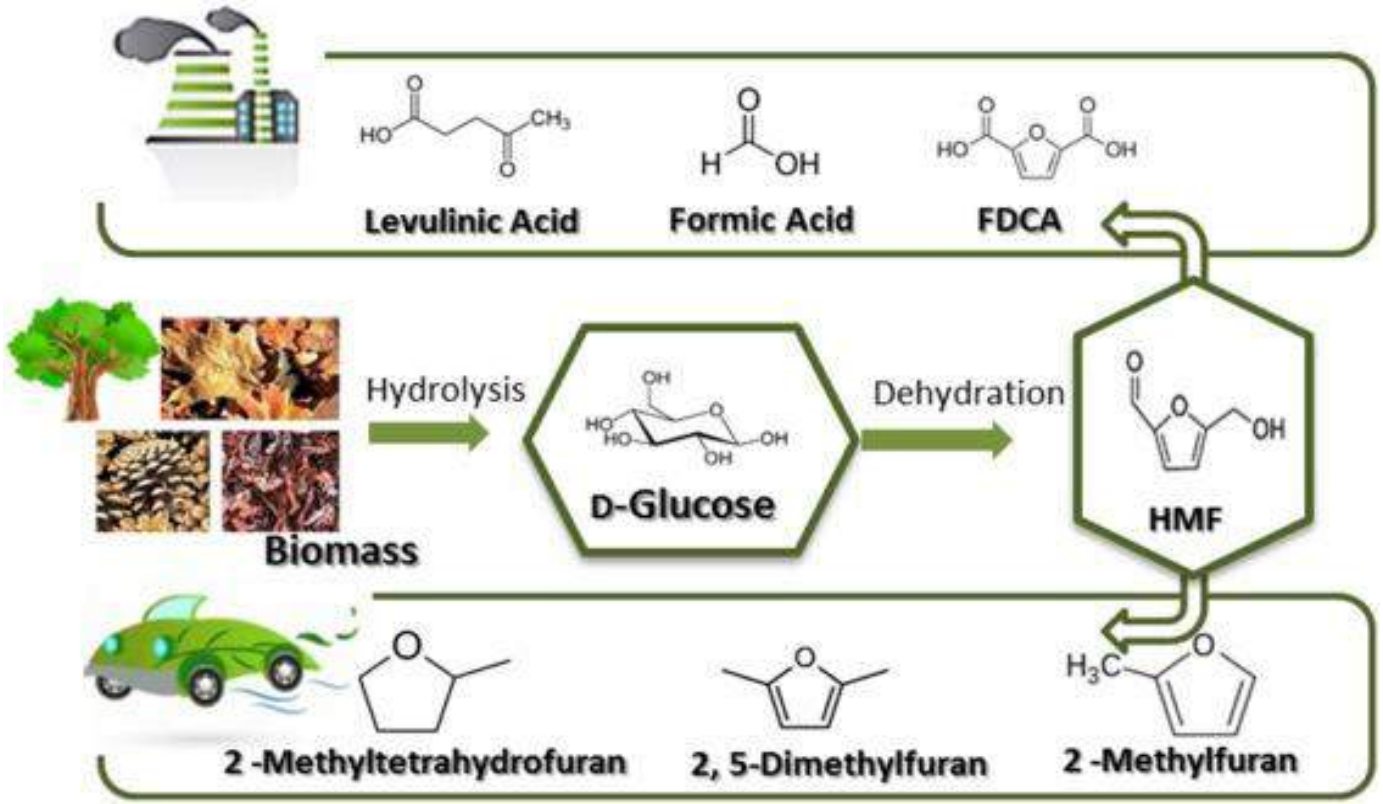
HMF



Enormous increase of the interest on HMF synthesis and use as platform chemical



R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. De Vries, *Chem Rev.* **2013**, *113*, 1499.


Levulinic Acid
Formic Acid
FDCA
Hydrolysis
D-Glucose
Dehydration
HMF
Biomass
2 -Methyltetrahydrofuran
2, 5-Dimethylfuran
2 -Methylfuran

The synthesis of HMF in water shows remarkable problems such as the formation of rehydration acids (levulinic acid and formic acid) and of solid by-products called humins. **Up to now very low yields were reached for substrate concentrations > 10 wt %!**

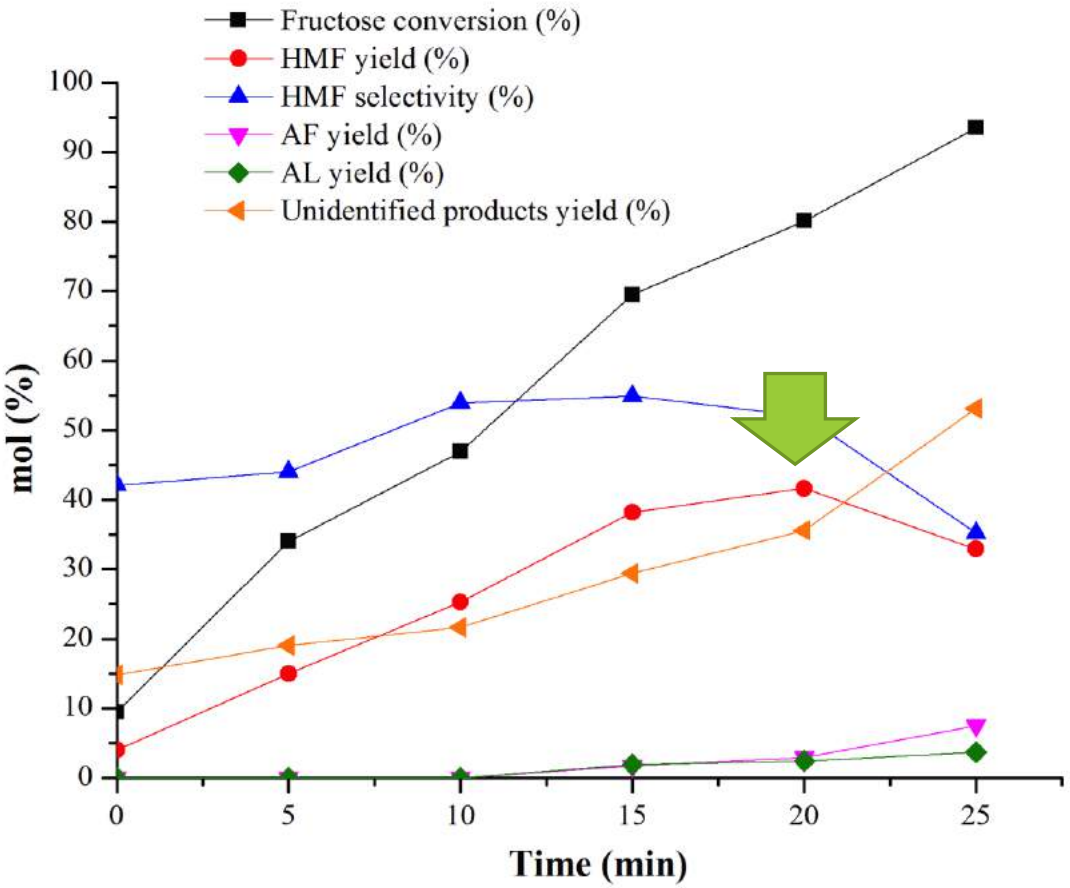
Now the reaction has been carried out in the respect of the Green Chemistry principles using water as solvent, microwave or traditional heating in the absence of catalysts or adopting a very low amount of heterogeneous catalyst. It is remarkable that high yields in HMF (up to 45 mol %) were reached working on concentrated biomass solutions (up to 30 wt. %).

Different starting substrates were adopted: raw sugars, cellulose, sugar syrups, waste cellulose, fruit peels …

C. Antonetti, M. Melloni, D. Licursi, S. Fulignati, E. Ribechini, S. Rivas, J.C. Parajó, F. Cavani, A.M. Raspolli Galletti, *Applied Catalysis B: Environmental* **2017**, *206*, 364-377.

For the first time very low amount of heterogeneous catalyst have been adopted

Kinetic study of fructose dehydration at 180 °C with Substrate/Amberlyst=79 wt/wt



Substrate: fructose **30 wt.%**

AUTOCATALYTIC!!!

Traditional heating

#Prova	1	2	3	4
TIME (min)	10	20	40	60
Conversion fru (%)	36,88	49,37	75,11	94,12
Selectivity glu (%)	1,15	1,72	1,05	0,65
Yield glu (%)	0,42	0,85	0,79	0,61
A.F. (g/l)	-	-	9,39	13,34
Selectivity A.F (%)	-	-	11,41	12,94
Yield A.F (%)	-	-	8,57	12,18
Selectivity A.L. (%)	-	-	3,57	6,80
Yield A.L. (%)	-	-	2,68	6,40
Selectivity HMF (%)	2,77	16,77	38,65	34,32
Yield HMF (%)	1,02	8,28	29,03	32,30
Others (%)	35,44	40,24	42,61	54,81

MW heating

#Prova	5	6	7	8
TIME (min)	5	10	15	20
Conversion fru (%)	73,35	88,87	99,11	99,24
Selectivity glu (%)	1,35	1,07	0,28	0,29
Yield glu (%)	0,99	0,95	0,28	0,29
A.F. (g/l)	6,85	10,25	13,02	14,55
Selectivity A.F (%)	8,53	11,36	11,99	13,39
Yield A.F (%)	6,26	10,10	11,88	13,29
Selectivity A.L. (%)	1,23	2,61	7,45	8,71
Yield A.L. (%)	0,90	2,32	7,39	8,64
Selectivity HMF (%)	36,47	43,39	22,56	17,07
Yield HMF (%)	26,75	38,56	22,36	16,93
Others (%)	44,71	47,04	69,08	73,38

The process was the optimized for different starting substrates such as raw sugars, waste cellulose, sugar syrups, fruit peels .

ALSO FOR THESE MATERIALS FOR THE FIRST TIME REMARKABLE YIELDS IN HMF WERE OBTAINED WORKING AT HIGH CONCENTRATION (up 30 wt %).

AUTOCATALYSIS AFFORDED EXCELLENT PERFORMANCES!!!

GREEN TANNING

HMF solution

Tanning Agents, Eur. Patent 3169816A1 (to University of Pisa, Po.Te.Co. and ARCHA S.r.l.)

Tanning experiments using raw hydrolyzates

The obtained aqueous solutions were directly employed as tanning agents WITHOUT ANY PURIFICATION

The interaction between “tanning hydrolyzates” and skin were investigated considering:

- shrinkage temperature
- process pH

Tanning with the solution as deriving from **autocatalytic** conversion: ΔTg **at** pH 7: **+ 23 °C**

- ✓ Good interaction between tanning agents and skin
- ✓ Good fatliquors penetration and fibres lubrification
- ✓ Light brown color of tanned leather, satisfactory tinctorial versatility

Lamb skin pickled : Tg 48 °C.

Tanning with the solution deriving from catalytic conversion: ΔTg at pH 7: + 23 °C

Organoleptic properties of crust leather:

- ✓ High softness
- ✓ Good fullness and roundness
- ✓ Goog dyeability

The optimization of this process now is in progress.

The results were recently patented and open the way to a new class of locally sourced vegetable tanning agents "farm to industry" which do not involve deforestation or importing from distant countries.

Tanning Agents, Eur. Patent 3169816A1 (to University of Pisa, Po.Te.Co and ARCHA S.r.l.).