# FROM TANNERIES SOLID WASTE TO CATALYSIS

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**ABSTRACT**

It is estimated that leather processing produces 200 times more waste than total product output thus negatively impacting in the environment.[1] Waste from tannery industries are solids or liquids. While liquid waste management has been widely and successfully explored with several good practices already applied in industrial scale,[2] solid wastes are usually used to produce fertilizers, gelatin, biogas and other products that actually found a limited practical application beyond academic speculations.[1] In our very innovative ongoing project, we are focusing our attention on solid wastes from both traditional and vegetal tanned leather with a particular attention to split offcut, shaving and leather dust materials with the idea to use them for the production of high valuable products and catalysts with no further waste production. Starting from vegetable tanned leather split offcuts, tannins were firstly extracted by using sustainable solvents to be evaluated for their antioxidant activity for a possible application in cosmetic. The residual biomass and leather offcuts from Cr based tanning have been micronized with different techniques (*i.e.* ball mill, mixer) and evaluated as additives for the microwave-assisted hydroformylation[3-4] of allylbenzene in water. Preliminary results show that micronized leather samples differently impact in the regioselectivity and efficiency of the overall process. Tuning the reaction conditions is possible to selectively obtain the linear aldehyde or alcohol depending on the reaction temperature and on the water/leather ratio. The catalyst and the leather can be recovered and reused several times without affecting reaction yields.

*Keywords: catalysis, green chemistry, tanneries solid waste valorization, microwave assisted organic synthesis*

## 1. Introduction

Italy is historically a world leader in tanning industry (65% at EU level, 25% of global production)[1] producing a large amount of waste that need to be managed taking inspiration from circular economy and green chemistry principles. The leather industry in Tuscan area involves the 28% of the national total being characterized by a high degree of craftsmanship and flexibility of their production, primarily focused on high fashion. In this district, the processes mainly concern medium and small size bovine hides, with leader industries in vegetal tanning area as well.[1] A 27% contraction in the Italian tanneries market has been observed because of the general uncertainties in the global economic situation during the COVID-19 pandemic. However, this has not prevented the Italian tanneries from confirm their high commitment to investments in sustainability, which exceed 4% of total turnover. As reported in UNIC report "*this strategy will prove to be even more important to intercept the opportunities for recovery from the crisis caused by the spread of the Covid-19 pandemic worldwide, which has abruptly and radically introduced changes in people's lifestyles and in the priorities of economic systems, putting even more at the center of the objectives of the supply chain the themes of competitiveness based on the criteria of sustainable development*".[1] As recently reported by Chojnacka and coworkers "*it is estimated that leather processing produces 200 times more waste than total product output*"[2] thus negatively impacting in the environment. Sustainability

in tanning requires a holistic approach covering technical, economic, environmental, social, institutional and legislative aspects,[1] and urgently requiring new approaches to waste recycling and valorization towards a more sustainable leather production. Most of

the purposed methods in the literature are focused on the management of heavy metals, azo dyes, phthalates and other chemicals. Waste from tannery industries are solids or liquids. While liquid waste management has been widely and successfully explored with several good practices already applied in industrial scale,[3] solid wastes are usually used to produce fertilizers, gelatin, biogas and other products that actually found a limited practical application beyond academic speculations.[2] In recent years, we start to investigate the valorization/ recycling of waste-derived materials (*i.e.* pine needles,[4] wool[5]) as support for heterogeneous catalysts in line with a biomass valorization in a circular economy approach. Moreover waste-derived materials are usually obtained from classical vegetal biomasses. In our very innovative ongoing project with Concerie La Bretagna S.r.l. and FGL International SPA, we are focusing our attention on solid wastes from tanned leather with a particular attention to split offcut, shaving and leather dust materials with the idea to use them for the production of high valuable products and catalysts with no further waste production. In our very innovative idea, we would like to valorize the overall waste lather biomass material in a really zero waste philosophy.[6] As an example, leather derived from vegetal tanning potentially contain tannins derivatives that can be extract and used as valuable products for cosmetic purposes before applying the residual biomass for different proposes (see Results and Discussion).

We decide to focus our attention on the use of both vegetable and classic Cr-based tanned leather off- cuts evaluating the impact of the biomass and of its treatment in different transformations. We here report only the application of vegetable tanned leather offcuts (VTLOCs) as auxiliary/support for metal based catalytic processes as at this stage the application of the Cr-based biomasses is in a very preliminary stage giving better results in other transformations than hydroformylation (HF). We decide to investigate the use of VTLOCs on the most applied industrial catalytic process: hydroformylation (HF) reaction.[7] In this case, we use the leather offcuts as auxiliaries only after the extraction of tannins residues that are evaluated for their antioxidant activity and possible applications as additive in cosmetics. The HF reaction, frequently called oxo process, is the most applied catalytic process allover the world.[8] Looking at the 12 principle of Green Chemistry as a model to generally establish the greenness of a process,[9] HF reaction is a very atom economic catalytic process lacking of several other points (Figure 1). Very hard reaction conditions in term of temperature (higher than 100 °C), times (24- 72 h), and syngas pressures (10-100 bar) as well as not properly ecofriendly solvents as toluene or tetrahydrofurane (THF) are required indeed.[7-8] During the years, we worked in improving the overall sustainability of the HF reaction by using microwaves as energy source[10] and more recently exploring micellar catalysis to work in more ecofriendly media such as water.[11] In this context, we decide to evaluate the possible use of VTLOC as an auxiliary in HF reaction able to replace the surfactants used in our micellar catalyzed protocol and letting the transformation happen in water. We here report our very preliminary data in the optimization of HF protocol.

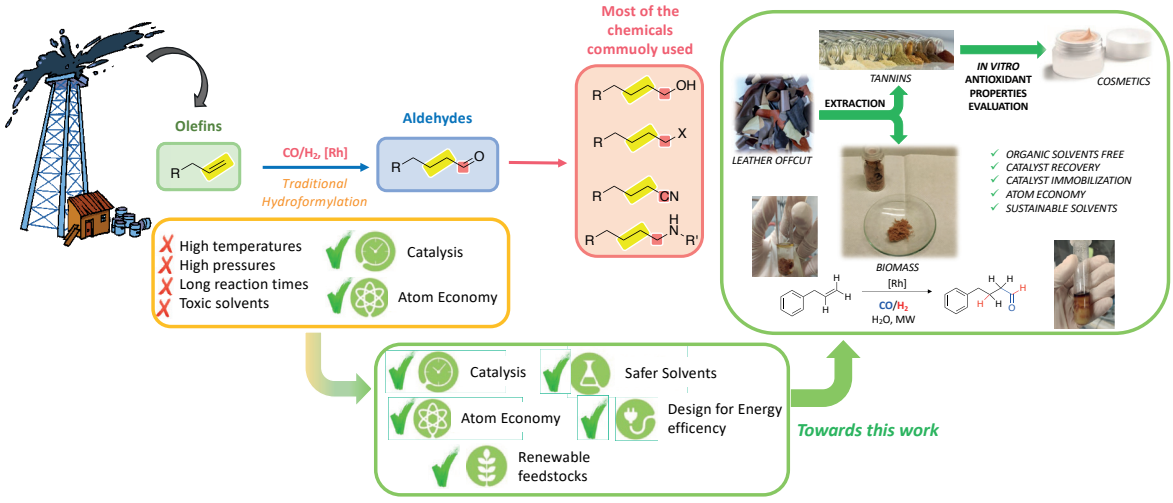



*Figure 1*

## 2. Material and Methods

All reagents were used as purchased from commercial suppliers (i.e. Merk for surfactant and ligand, TCI for Rh catalyst) without further purification. Flash column chromatography was performed in glass columns using Merk silica gel 60 Å, 230-400 mesh particle size Merck aluminum backed plates pre- coated with silica gel 60 (UV254) were used for analytical thin-layer chromatography and were visualized by staining with a solution *p*-anisaldehyde in EtOH or a $KMnO_4$ solution. $^1H$ NMR, and $^{13}C$ spectra were recorded on 400 MHz, 600 MHz, and 243 MHz Brücker Advance NMR spectrometers. Deuterated chloroform and methanol were used as the solvents and chemical shift values (δ) are reported in parts per million (ppm) referring to the residual signals of the deuterated solvent (δ 7.26 for $^1H$ and δ 77.6 for $^{13}C$ in $CDCl_3$, δ 3.34 for $^1H$ and δ 49.00 for $^{13}C$ in $CD_3OD$). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t

= triplet, q = quartet, m = multiplet or multiple resonances, bs = broad singlet), coupling constant (*J*) in Hertz and the integration in ppm. Mass spectrometry data were collected on Varian Saturn 2000 GC/MS spectrometer with ion trap detector and equipped with 30 m OV-101 capillary column, splitting injector at 240 °C. Methods for GC analysis: 40 °C - 3 min, 40-200 °C 10 °C/min – 17 min, 200-240 °C 20

°C/min – 5 min; B) 40 °C - 3 min, 40-200 °C 10 °C/min – 1 min, 200-240 °C 20 °C/min – 8 min, 240- 280 °C 20 °C/min, 8 min. Reactions carried out under MW dielectric heating were performed with a modified Discover microwave oven equipped with the 80 mL vial for reaction under pressure.[10] *General method for HF to aldehyde*: A 80 mL MW tube was charged with $H_2O$ (3 mL) and alkene (2.25 mmol, 0.75 M solution). Then VTLOC (84 mg), $Rh(CO)H(PPh_3)_3$ (21 mg, 0.0225 mmol) and Xantphos (52 mg, 0.09 mmol) were added. The yellow suspension was stirred for 5 minutes under $N_2$. The mixture was subjected to 3 cycles of vacuum/syngas inside the microwave cavity. Syngas was added since 130 psi (9 bar) are detected, and irradiated at 80 °C for 40 minutes cooling while heating with a fixed power of 300 Watt. After irradiation the mixture was cooled-down to room temperature and the internal gas released by opening the external pressure valve. The mixture was filtered on Büchner washing with EtOAc (5 mL). EtOAc phase was dried with dry $Na_2SO_4$, filtered, evaporated under reduced pressure and analyzed by GC/MS or $^1H$- and $^{13}C$-NMR after column chromatography purification, furnishing the desired aldehyde. Water phase and recovered VTLOC were reused by adding only the starting alkene at least for 3 times without affecting reaction yields and regioselectivities.

**4-(3,4-Dimethoxyphenyl)butanal (2a)**. The title compound was obtained starting from 4-allyl-1,2-dimethoxybenzene. **Yield**: 46%. **GC/MS (m/z)**: 208; $R_t$ =18.3 min. **$^1H$ NMR** (600 MHz, $CDCl_3$): o 9.76

(s, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 9.1 Hz, 1H), 6.70 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.61

(t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.95 (p, *J* = 7.3 Hz, 2H). **$^{13}C$ NMR** (151 MHz, $CDCl_3$): o

202.4, 148.9, 147.4, 133.9, 120.3, 111.7, 111.3, 56.0, 43.1, 34.6, 23.8. Elemental analysis calcd. for

$C_{12}H_{16}O_3$: C, 69.21; H, 7.74; O, 23.05. Found: C, 69.17; H, 7.72.

**Nonanal (7)**. The title compound was obtained starting from 1-octene. **Yield**: 78%. **GC/MS (m/z)**: 142; $R_t$ = 10.8 min. **$^1H$ NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 1.8 Hz, 1H), 2.38 (td, *J* = 7.3, 1.7 Hz, 2H),

1.61–1.57 (m, 2H), 1.26–1.23 (m, 10H), 0.84 (t, *J* = 6.3 Hz, 3H). **$^{13}C$ NMR** (100 MHz, $CDCl_3$) δ 203.1,

44.0, 31.9, 29.4, 29.3, 29.2, 22.8, 22.2, 14.2.

*General method for HF to alcohol*: A 80 mL MW tube was charged with $H_2O$ (3 mL) and alkene (2.25 mmol, 0.75 M solution). Then VTLOC (42 mg), $Rh(CO)H(PPh_3)_3$ (21 mg, 0.0225 mmol) and Xantphos (52 mg, 0.09 mmol) were added. The yellow suspension was stirred for 5 minutes under $N_2$. The mixture was subjected to 3 cycles of vacuum/syngas inside the microwave cavity. Syngas was added since 150 psi (10 bar) are detected, and irradiated at 110 °C for 40 minutes cooling while heating with a fixed power of 300 Watt. After irradiation the mixture was cooled-down to room temperature and the internal gas released by opening the external pressure valve. The mixture was filtered on Büchner washing with EtOAc (5 mL). EtOAc phase was dried with dry $Na_2SO_4$, filtered, evaporated under reduced pressure and analyzed by GC/MS or $^1H$- and $^{13}C$-NMR after column chromatography purification, furnishing the desired alcohol. Water phase and recovered VTLOC were reused by adding only the starting alkene at least for 3 times without affecting reaction yields and regioselectivities.

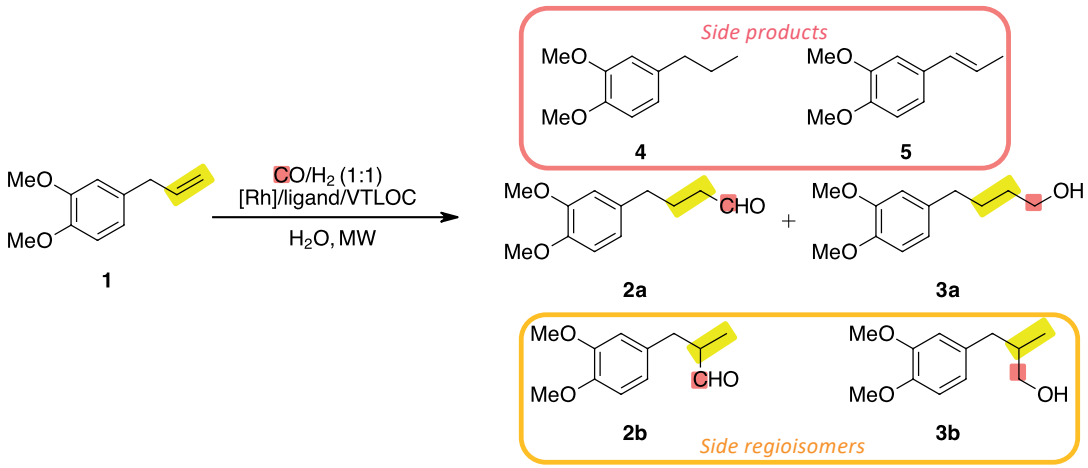
**4-(3,4-Dimethoxyphenyl)butanol (3a)**. The title compound was obtained starting from 4-allyl-1,2-

dimethoxybenzene. **Yield**: 90%. **GC/MS (m/z)**: 208; $R_t$ =20.1 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.79 (d, J = 8.6 Hz, 1H), 6.77-6.62 (m, 2H), 3.86 (s, 3H), 3.90 (s, 3H), 3.71-3.60 (m, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 1.75-1.55 (m, 4H), 1.25 (br s, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 148.7, 147.0, 134.5, 120.3, 111.7, 111.1, 62.9, 55.8, 55.6, 35.3, 32.3, 27.7.

**Nonanol (8)**. The title compound was obtained starting from 1-octene. **Yield**: 96%. **GC/MS (m/z)**: 142; $R_t$ = 11.3 min. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.54 (t, *J* = 6.7 Hz, 2 H), 2.41 (s, 1 H), 1.53 – 1.44 (m, 2 H), 1.28 – 1.17 (m, 12H), 0.81 (t, *J* = 6.8 Hz, 3 H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 62.7, 32.8, 31.6, 29.9, 29.4, 29.2, 25.7, 22.6, 14.0.

## 3. Results and Discussion

As VTLOCs are rich in tanning with potentially interesting biological properties, we firstly grind VTLOCs and extract tannins by using EtOH (ecofriendly solvent). The evaluation of the antioxidant activity of the extract is ongoing in Prof Annalisa Santucci's laboratory at the University of Siena.




| Entry | Conditions | VTLOC/Cat. | Conv% | | |
|---|---|---|---|---|---|
| | | | 2 (2a/2b) | 3 (3a:3b) | 5 |
| 1 | $CO/H_2$ (11 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, 2.5%wt TPGS-750M, $H_2O$, MW, 80 °C, 40 min | - | 76 (2:1) | - | 10 |
| 2 | $CO/H_2$ (11 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, VTLOC, $H_2O$, MW, 80 °C, 40 min | 2:1 | 28 (6:1) | - | 70 |
| 3 | $CO/H_2$ (9 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, VTLOC, $H_2O$, MW, 80 °C, 40 min | 2:1 | 14 (n.d.) | | 85 |
| 4 | $CO/H_2$ (9 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, VTLOC, $H_2O$, MW, 80 °C, 40 min | 4:1 | 42 (1:0) | | 58 |
| 5 | $CO/H_2$ (9 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, VTLOC, $H_2O$, MW, 110 °C, 40 min | 4:1 | 27 (8:1) | | 51 |
| 6 | $CO/H_2$ (10 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, VTLOC, $H_2O$, MW, 80 °C, 40 min | 4:1 | 46 (11:1) | | 50 |
| 7 | $CO/H_2$ (10 bar) $Rh(CO)H(PPh_3)_3$/Biphephos, VTLOC, $H_2O$, MW, 80 °C, 40 min | 4:1 | 31 (4:1) | | 62 |
| 8 | $CO/H_2$ (10 bar) $Rh(CO)_2$acac/Xantohos, VTLOC, $H_2O$, MW, 80 °C, 40 min | 4:1 | 15 (5:1) | | 30 |
| 9 | $CO/H_2$ (10 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, $H_2O$, MW, 80 °C, 40 min | - | 10 (6:1) | | 65 |
| 10 | $CO/H_2$ (10 bar) $Rh(CO)H(PPh_3)_3$/Xantohos, VTLOC, $H_2O$, MW, 110 °C, 40 min | 2:1 | - | 90 (11:1) | 5 |

*Table 1*

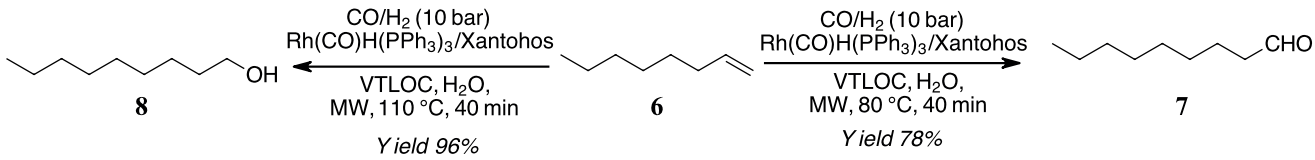
The residual biomass has been used to replace the surfactant TPGS-750M (Table 1, entry 1) catalyzed HF reaction protocol in $H_2O$.[11] We decide to use eugenol (**1**) as model compound: applying the standard conditions developed for micellar catalyzed HF ($CO/H_2$ (11 bar), $Rh(CO)H(PPh_3)_3$/Xantohos, $H_2O$, MW, 80 °C, 40 min) and introducing VTLOCs in 2:1 ratio with respect the catalyst, the expected aldehyde **2** was obtained in poor conversion with **5** (double bond isomerization) as the main reaction product (Table 1, entry 2).

Even worst results were observed by lowering the syngas pressure to 9 bar (Table 1, entry 3). A real improvement in both conversion and regioselectivity was observed by changing the VTLOC ratio to 4/1

(Table 1, entry 4). Higher temperature didn't help (Table 1, entry 5), while higher pressures (10 bar) of syngas consent to obtain expected aldehyde **2** in 46% isolated yields with a very good regioselectivity towards the linear isomer **2a** (Table 1, entry 6).

Changing the catalyst and the ligand, we couldn't obtain better results (Table, entry 7 and 8). Moreover, the exploration of different reaction conditions in term of pressure, temperature, time, catalysts, ligands, and their ratios will be necessary to optimize the overall process. It is interesting to note that the VTLOC material has an impact in the reaction outcome, as without VTLOC only a 10% of aldehyde was formed (Table 1, entry 9). Furthermore, irradiating with microwaves at 110 °C for 40 minutes, it was possible to obtain alcohol **3a** in 90% yield and very good regioselectivity (Table 1, entry 10). These data are really interesting as only few protocols are reported in the literature so far to directly obtain alcohols by using HF in really harder reaction conditions (130-140 °C, 40-60 bar, 20 h) and not ecofriendly solvents (NMP).[12-15] With our surprise, we are actually able to obtain homologous alcohols by olefins HF in water in very ecofriendly conditions thanks to the use of both microwave irradiation and the waste derived biomass represented by VTLOC.

Just to preliminary explore the general applicability of the proposed protocols, we applied the reaction conditions reported in entries 6 and 10 on 1-octene obtaining 1-nonal and 1-nonanol respectively in very good isolated yields and optimal regioselectivities (Scheme 1).




*Scheme 1*

Surprisingly, 1-octene demonstrate to be a better substrate for HF reaction with respect to eugenol furnishing the linear aldehyde in 78% isolated yields. In the workup of this reaction the use of organic solvents can be completely avoid as nonanal can be isolated as a pure compound just after centrifugation and phase separation. The recycling of VTLOC, water and catalyst is under investigation together with Life Cycle Assessment (LCA) analysis.

## 4. Conclusion

Here, we reported our preliminary data in the optimization of a zero waste protocol for the VTLOC based HF reaction on eugenol in water. During our preliminary studies we optimized an ecofriendly protocol for the preparation of alcohols by olefin hydroformylation.

This transformation is very interesting as few protocols are available so far, none using sustainable conditions. Further studies will be necessary to evaluate the catalyst/ligand recycle and the general applicability of the process.

More efforts will be needed for the optimization of the reaction conditions required to obtain aldehydes. Moreover, our preliminary data are very encouraging (46% yields and optima regioselectivity).

This is the first waste based protocol for the HF reported so far. The evaluation by LCA analysis of the impact of the proposed methodology both in the preparation of alcohols and aldehydes is ongoing.

The use of Cr-based tanned leather off-cuts is actually ongoing with promising preliminary results in oxidation reactions.

## 5. Acknowledgements

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**Note**