

Method to use hair from hair-preserving liming of tanneries for retanning

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ABSTRACT

During the production of leather, the structural protein of the hair - keratin - is produced as a significant by-product stream, which has hardly been utilised to date, but is disposed of in sewage treatment plants with energy expenditure or composted for a fee leading to an additional CO₂-release. It has not yet been utilised as a material. Preliminary work has shown that tanning agents and fillers, which are necessary to achieve specific properties of leather (e.g., tensile strength, elasticity, softness) in the retanning process, can also be produced from proteins. In our recent work we processed hair by partial hydrolysis, modification and further chemical processing on a pilot scale to make it usable as retanning agent and filler for leather. A production plant in a container that had already been designed, constructed and built for other applications is used for this purpose. First results on calculation the product carbon footprint for the new re-tanning and filling material showed a potential reduction by two to four times compared to fossil-based agents. The new retanning and filling agent is expected to be able to partly replace the currently non-biogenic components in leather production with locally sourced biogenic raw materials. It contributes to better utilisation of the by-products of animal breeding. Utilising the hair is a further step towards making leather even more sustainable, with the potential to achieve this worldwide.

Keywords: leather, by-product use, hair, retanning, sustainability

1. Introduction

Leather is a strong, flexible, and durable material derived from the chemical processing of animal hides with properties that are not yet achieved by alternative materials (Meyer et al., 2021). Increasing concerns regarding greenhouse gas emissions from cattle farming, of which leather is a by-product, and a sustainable production of the leather itself have led to continuous efforts in the search for improving the sustainability of leather production and minimising waste during the processing of hides (Gomes et al., 2020), (Prokein et al., 2017), (Colak, S. et al., 2005). The production of leather generates significant by-product streams in the form of off-cuts, splits, shavings and also keratin, the structural protein found in hair. De-hairing in industrial process can be carried out using a hair-preserving or a hair-destroying process. Both technologies require the use of sodium sulphide, whereby the concentrations used in the hair-destroying process are typically higher and may lead to sulphide concentrations in the effluent stream of up to 8.5 kg/t of salted cattle hides (Galarza et al., 2009). As beamhouse processes are responsible for about 18 % of the global warming potential of leather manufacture and over 40 % of freshwater ecotoxicity (Brugnoli et al., 2025), hair saving processes with its lower use of sulphide would be highly desirable, especially if the keratin in hair could be used as a valuable product (de Souza et al., 2022). However, until now, the keratin of bovine hair has been largely unused, instead being disposed of in sewage treatment plants at great expense or composted at a cost. It is not used as a material, partly because its high sulphur content and superstructure make it a complicated protein for material use.

Leather production today already largely dispenses with fossil raw materials. Leather is industrially produced with over 65% biological and therefore renewable content (Carcione et al., 2023), (Autenrieth et al., 2020). However, replacing the non-biogenic components currently in use with locally sourced

biogenic raw materials remains a challenge. Despite a wide variety of long known and also new vegetable tannins (Schröpfer and Meyer, 2016), (Mondschein et al., 2022), (China et al., 2020), petroleum-based products are still used for retanning and filling, which gives leather many of its desirable properties, such as high tear resistance, high elasticity and good softness. Retanning agents and fillers are a very heterogeneous group of derivatives of mostly condensed hydroxyphenyl compounds or polyacrylates (polymer tanning agents). Fillers such as polymer tanning agents, are purely synthetic products of fossil origin. They used to fill in loose areas of the skin, for example in the flanks. Fillers do not increase the denaturation temperature of leather and therefore do not tan, but they have a significant influence on the feel, fullness and water vapour absorption of a leather. Fillers are not a homogeneous group of chemical substances, but essentially large molecules up to particles. They can react with collagen and also with inorganic tanning agents and auxiliary substances, such as zeolites and chrome tanning agents (Reich, 1995). The transition between retanning agents and fillers is fluid and depends on derivatisation, molecule size, tanning effect and other potentially reactive components of the retanning system (Reich, 1996), (Covington, 2009).

Preliminary work has shown that the tanning agents and fillers can also be produced from proteins. By-products from leather production, e.g. shavings, can already be processed into retanning chemicals (Tegtmeyer, 2020). Industrial usability of keratin from the hair-preserving liming process used in tanneries, however, has not been explored so far. The potential of using this waste from the de-hairing process for leather retanning or filling will be explored in this paper.

2. Material and Methods

2.1. Preparation of retanning agent

Hair waste was used from an industrial tannery (HELLER-LEDER GmbH & Co. KG). The hair was used as received with a dry matter content of approx. 30%. Hydrolysis was performed using a 50 % (w/w) NaOH solution in water and subsequent enzymatic treatment with Peltec® X-Zyme U (TFL Ledertechnik GmbH). The resulting solution after hydrolysis contained 1 - 3 % solids and was used for graft-polymerisation with acrylic acid without further separation. For pH adjustment to neutral pH or below, sulphide residues need to be removed by hydrogen peroxide with a reaction time not less than 1h.

For grafting, 1500 grams of the keratin hydrolysate (33% w/w organic substance in water) were introduced into a 2 liter reactor. The content of the reactor was heated to 88 - 92 °C under stirring. 0.66 grams ammonium persulphate dissolved in 10 ml of distilled water was added and 5 minutes later 33 grams of acrylic acid were metered into the reactor. After curing for 3 hours the final product was obtained by allowing the reactor to cool to room temperature under stirring.

The ecological calculation was carried out within the cradle-to-gate system boundary and includes allocations from the current guidelines (Rosa-Giglio et al., 2018). The Ecoinvent database 3.9 and Umberto software were used as the data basis for chemicals. For the initial ecological assessment of the product, waste management was not yet included in the analysis and 100% of the energy used came from renewable sources. Energy consumption was measured on site.

2.2. Preparation of leather samples

The laboratory-scale retanning tests were carried out on wet blue pieces (chrome tanned cow skin, standard protocol) of approx. 200 g in a parallel dyeing machine (diameter approx. 50 cm). The grafted hydrolysates were tested at a ratio of 8 % dry organic substance of grafted hydrolysate. Hydrolysate without grafting was tested in comparison as well as a standard commercial filler (Tafigal HK, Zschimmer & Schwarz GmbH & Co KG). Pelt mass, treatment time and float volume were kept constant. Experiments with grafted hydrolysates were repeated in 1 m-diameter tanning drum (Dosemat).

2.3. Analytical methods

Characterisation of the dispersions

The determination of the molecular weight of the hydrolysed hair and the grafted protein solution was performed by GPC. A Superdex Peptide column with a separation range from: 100 Da – 7 kDa and an exclusion limit of 20 kDa was used. After dilution and filtration, the samples were automatically injected and separated chromatographically using an isocratic method (mobile phase composition: 0.15 M NaCl, 0.015 M NaH_2PO_4 , 0.035 M Na_2HPO_4 , flow: 0.5 ml/min flow, column temperature: 50 °C) and detected spectroscopically at 254 nm.

The dispersions were analyzed with respect to particle size and size distribution using an LUMiSizer 651 (LUM GmbH, Berlin). Spatially and temporally resolved transmission spectra were collected in PC cuvettes at a wavelength of 870 nm, a temperature of 25 °C, and a rotational speed of 4000 rpm. Data evaluation was performed using the SepView 6 software.

Percentage of tanning agents was determined according to DIN EN ISO 14088.

Leather Testing

For the determination of the temperature of denaturation, the re-tanned leathers were cut into pieces of appr. 10 mg (dry mass) and soaked in deionised water for 24 h. Samples were then placed in aluminium pans (pan volume 40 µl) and hermetically sealed. Temperature scans were run from 10 – 125 °C with a rate of 5 Kmin⁻¹. From the endotherms, T_{onset} and T_{peak} were calculated.

Tensile strength and elongation were performed according to DIN EN ISO 3376, and tear propagation load was performed according to DIN EN ISO 3377-1. Stitch tear resistance was determined according to DIN EN ISO 23910.

3. Results and Discussion

The partial hydrolysis of keratin and its subsequent derivatisation into a retanning or filling agent was tested in lab scale. The procedure followed an alternative concept of using shavings from the thickness adjustment of leather during processing (Song, 2012). However, shavings might be used as well in higher value applications, such as leather board, the waste keratin from bovine hair was tested as cheaper alternative. Hydrolysis was carried out to obtain a soluble or dispersed protein material that can be pumped in industrial processes. The optimal process included both an alkaline treatment as well as an enzymatic treatment. The molecular weight of the soluble keratin hydrolysate was investigated by GPC. The results are given in Figure 1. Enzymatic treatment as well as the oxidising activity of the hydrogen peroxide both reduce the percentage of higher molecular weight keratin fragments. The main peak is at around 280 Da, which corresponds to fragments of 2–3 amino acids.

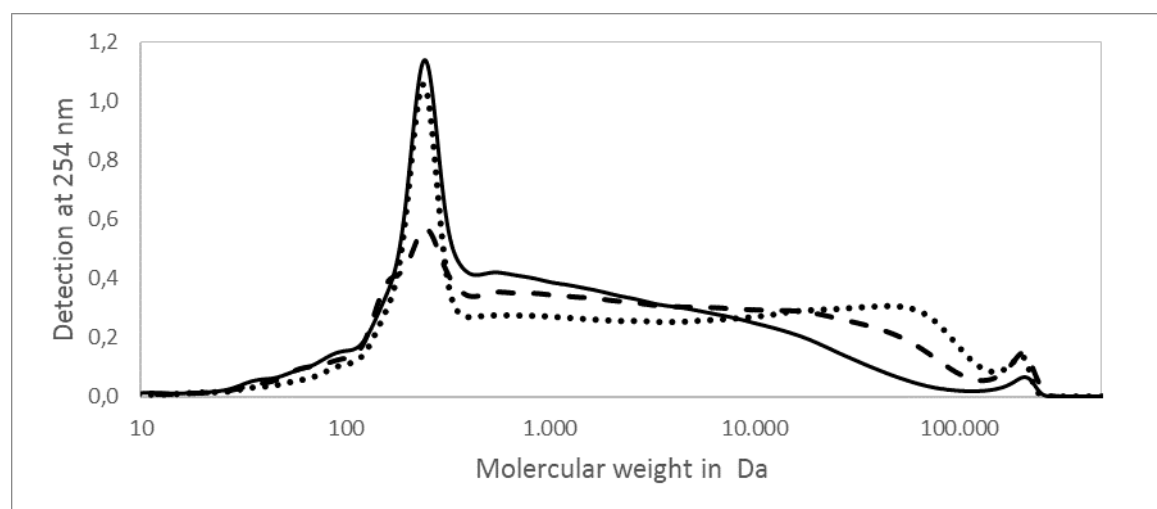


Figure 1: GPC of the soluble fraction after hydrolysis of keratin with NaOH, 1 h hydrogen peroxide (dotted line), after NaOH, enzymatic treatment, 1 h hydrogen peroxide (dashed line) and NaOH and enzymatic treatment, 2 h oxidation with hydrogen peroxide (solid line).

After the grafting reaction, the pronounced peak at approximately 280 Da disappears, indicating a reaction with these fragments, which leads to higher molecular weights (Figure 2). The reaction depends on the pH of the reaction mixture.

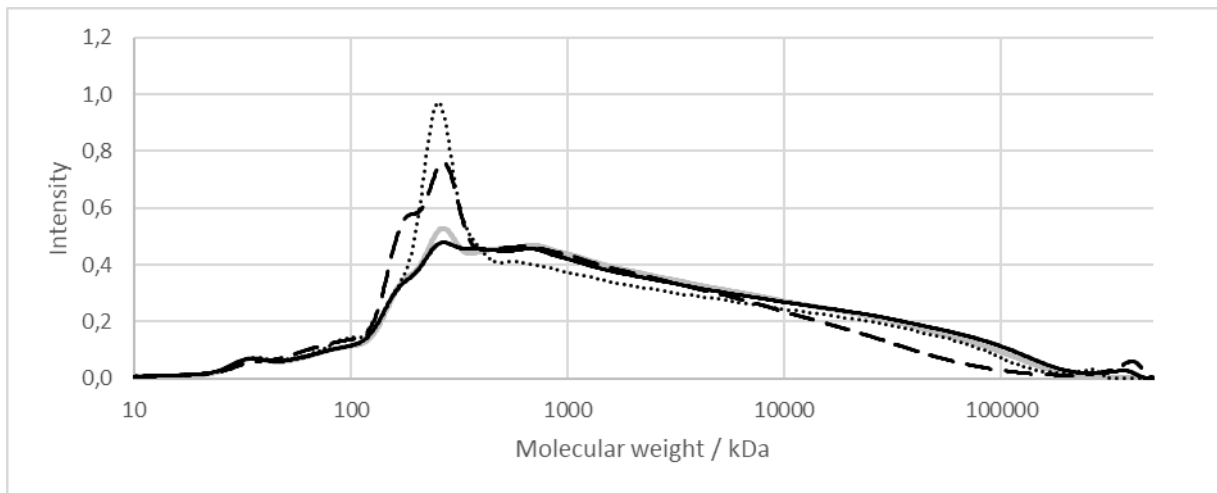


Figure 2: GPC of the soluble fraction of hydrolysed keratin after grafting with acrylic acid. Grafting reaction at pH 5.5 (solid line), pH 7.6 (grey line), pH 8.5 (dashed line) and hydrolysate without grafting (dotted line).

The hydrolysate and grafted reaction products were further characterised regarding the particle size. Measured particle size is between 0,1 and 100 μm , showing a slight shift to higher values from hydrolysed protein fragments to the grafted reaction product (see Figure 3).

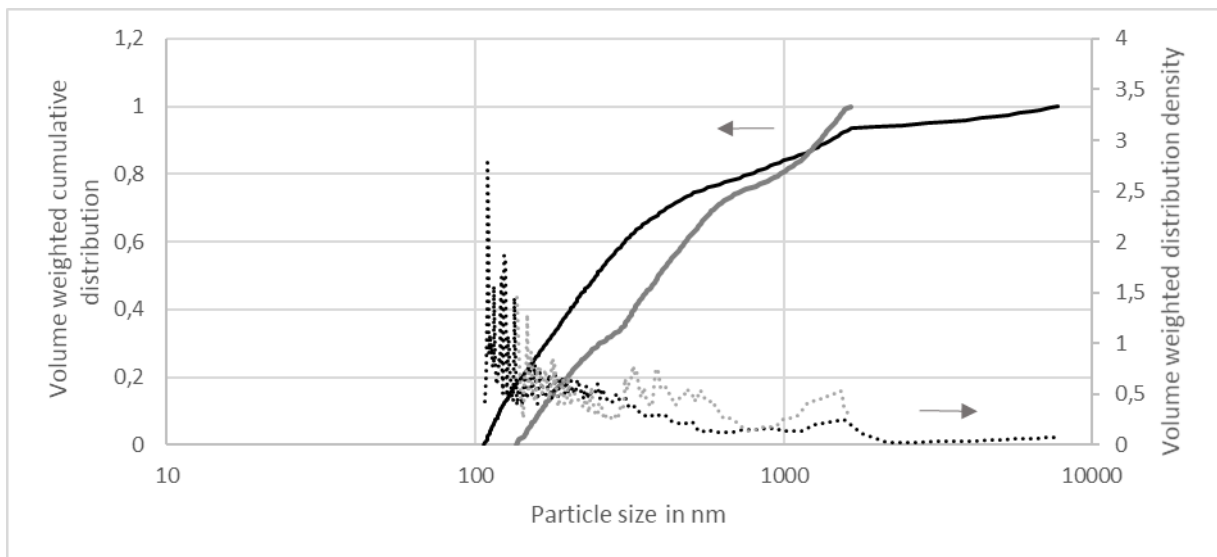


Figure 3: Particle size analysis of dispersions of hydrolysate (black) and grafted product from reaction at pH 7.6 (grey). Volume weighted cumulative distribution: solid lines, distribution density: dotted lines.

The investigation of the tanning ability of the product according to DIN EN ISO 14088 (filter bell method) resulted in a ratio of tanning active content to non-tanning content of below 0.1, which characterises the product as a filler rather than a retanning agent. Accordingly, leather treated with the grafted product did not show a shift in the denaturation temperature determined by DCS measurement.

Leathers with the grafted product in the retanning process were prepared in lab scale. Beside the grafted keratin hydrolysate, a commercial polymer retanning agent (Tafigal HK) and the keratin hydrolysate

without further treatment were used as reference. First experiments show that tensile strength is between 11 and 15 MPa, it does not significantly differ between the commercial retanning agent, the keratin hydrolysate and the grafted hydrolysate treated samples due to the overlapping failure margins. Elongation at break is reduced for the keratin hydrolysate treated sample (see Figure 4). Stitch tear resistance is increased for both the keratin hydrolysate as well as the grafted keratin hydrolysate compared to the commercial reference. For tear propagation load, the values for the graft keratin hydrolysate treated leather are significantly higher compared to the hydrolysate treated and the reference treated with the commercial retanning agent (see Figure 5).

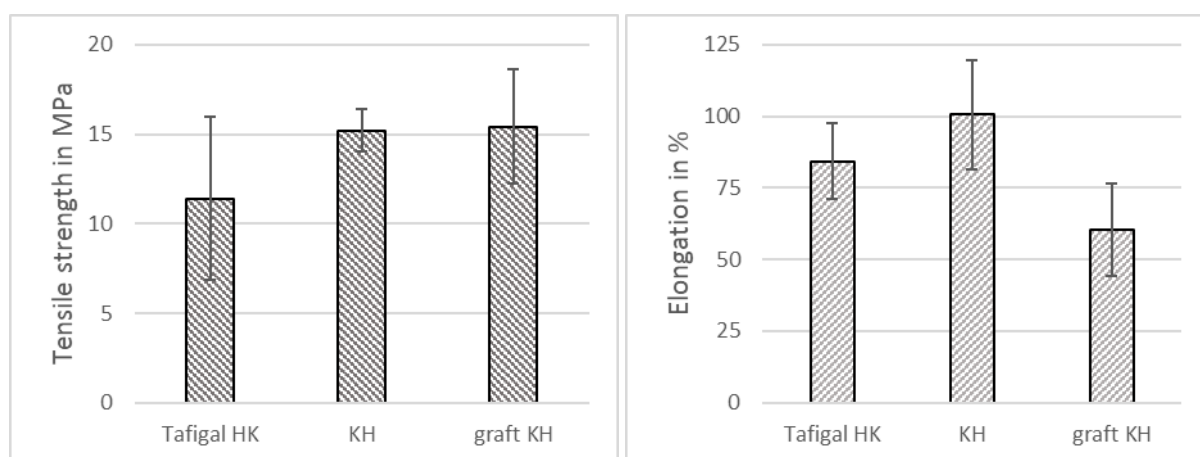


Figure 4: Tensile strength (left) and elongation at break (right) for retanned leather with a commercial retanning agent (Tafigal HK), hydrolysed keratin from hair (KH) and grafted keratin hydrolysate (graft KH).

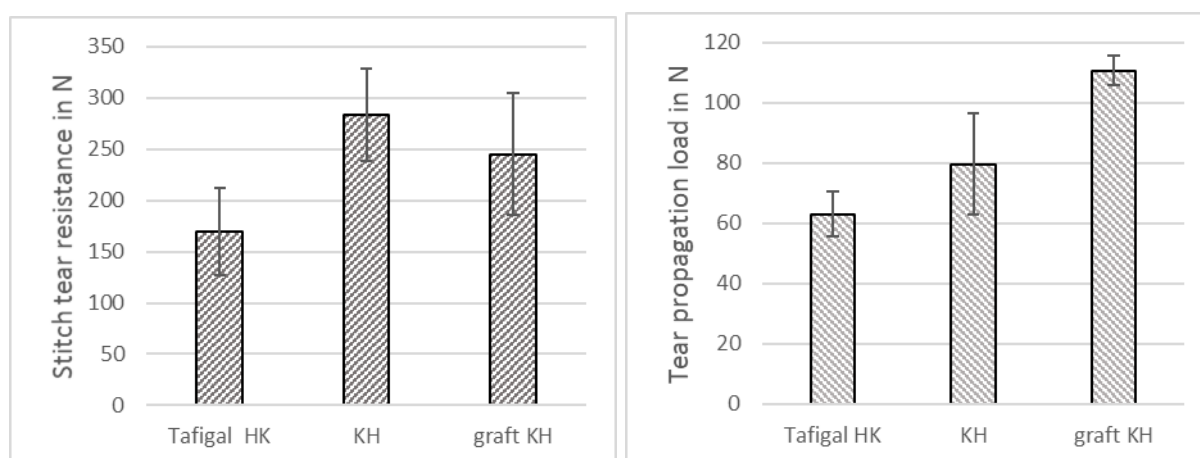


Figure 5: Stitch tear resistance (left) and tear propagation load (right) for retanned leather with a commercial retanning agent (Tafigal HK), hydrolysed keratin from hair (KH) and grafted keratin hydrolysate (graft KH).

In laboratory scale, the polymeric keratin from hair could be converted into retanning agents and fillers for leather through partial hydrolysis, modification and chemical processing, thereby making it industrially usable. Work with keratin is now being scaled up to industrial level. For this purpose, a production plant in a container is used, which had already been designed, engineered and built for other applications. The container can be used to produce a product from the by-products of leather production at the point of origin. The possibility of decentralised production within this concept eliminates a lot of transportation and packaging efforts, making this alternative adaptable to different requirements. The verification of the concept of a quasi-in-house chemical plant at the tannery, which the tanner then uses just in time in his leather production, eliminates all transport and packaging to a central chemical site

and back to the tannery, and only the quantities required for the leather manufacturing process need to be produced.

Since this method makes it significantly cheaper to use leather production waste as a raw material, it should result in an ecologically and economically interesting potential for recycling product streams. A product carbon footprint for the retanning/filling agent was calculated from the first trials at the industrial container equipment. The carbon footprint of the complete process with allocation from livestock farming ranges from 4.5 to 6.3 kg CO₂equivalent/kg product. This is remarkably higher compared with synthetic tanning agents based on fossil fuels that ranges between 0.88 and 2.25 kg CO₂equivalent/kg product for liquid agents (depending on concentration and product composition, data from TFL). However, if the core process (including allocation from beamhouse, hydrolysis and grafting) without allocation from cattle breeding is considered, calculation results in a significantly lower product carbon footprint of 0.35 kg CO₂equivalent/kg product compared to the polymer tanning agent. This means that the post-tanning agent has a greenhouse gas reduction potential of at least 50 % for the core process compared to fossil-based retanning agents, if these can be completely replaced.

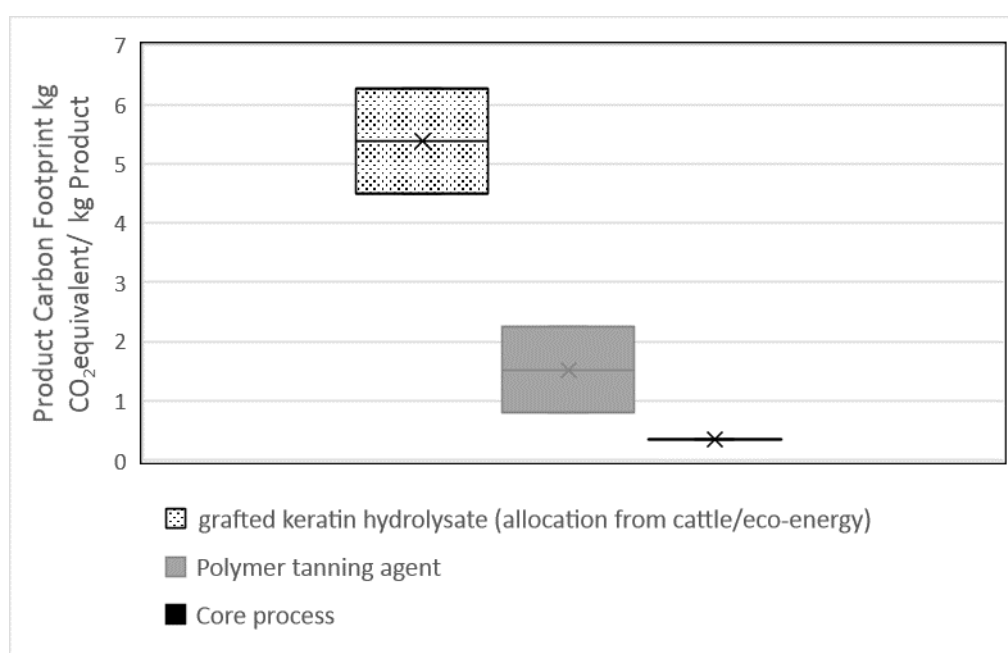


Figure 6: Product carbon footprint for the grafted keratin hydrolysate, including allocation from livestock farming, conventional polymer retanning agents and the core process of the grafted keratin hydrolysate (allocation from dehairing, keratin hydrolysis and grafting).

4. Conclusion

Due to its biogenic origin and durability, leather has significant advantages over fossil-based materials. Increasing the biogenic content in retanning will add to sustainability of leather products. Using the hair that comes from leather production as a material for retanning agents for leather production would help to increase the biogenic content and replace fossil constituents. As shown from the first trials, the core process for this keratin based retanning agent would reduce greenhouse-gas emissions. In addition, the planned use of the hair will reduce the amount of nitrogenous compounds in the atmosphere, as composting releases up to 45% of bound nitrogen as ammonia (Körner, 2009). If we further take into account that the hair is not converted into CO₂, water and N compounds during composting, but remains bound in the leather, it can be recorded as a defined sink for CO₂ that is removed from the global cycle for the useful life of the leather. The assumed useful life of leather varies between 1-3 years for shoe leather and at least 10 years for upholstery leather, accessories, etc. (Anonymous, 2020). This aspect is relevant for a possible estimation and assessment of the greenhouse gas reduction potential during the

use phase of the leather. However, a reliable calculation and balancing based on kg of chemical or m² of leather is only possible after scaled tests have been carried out and the end products manufactured (e.g. shoe or furniture leather) have been determined.

In summary, the upscaled process conserves fossil resources by using hair and replaces them with biogenic waste materials, which are avoided and used instead. The greenhouse gas reduction potential is substantial and new value chains can be created.

5. Acknowledgements

This work was carried out as part of a cooperation project funded by the Federal Ministry for Economic Affairs and Energy (13BDA70010) via VDI Technologiezentrum GmbH in accordance with a resolution of the German Bundestag. We would like to express our gratitude for the support provided.

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VDA 230-209 (09/2022).