Carolina Scaraffuni Gomes[1]
Jens-Uwe Repke[2]
Michael Meyer[1]

FILK Forschungsinstitut Leder und Kunststoffbahnen

PRE-TREATMENT TECHNIQUES OF CROSS-LINKED COLLAGEN TO DENATURE THE NATIVE STRUCTURE

INTRODUCTION

Leather shavings are crosslinked collagen residues produced in the leather industry which are very stable towards high temperatures and enzymatic degradation. This stability is due to natural cross-links in the collagen structure and chemical cross-links between collagen fibers formed in the tanning step in tanneries with chromium salts. In order to denature the native structure, enable enzymatic degradation to produce biogas, and speed up the biogas production different thermal and mechanical pre-treatments were carried out.

METHODS AND MATERIAL

PRE-TREATMENTS OF LEATHER SHAVINGS

AUTOCLAVING:

Moistened leather shavings were placed in screw cap micro tubes tightly closed through O-ring sealing and heated to 120°C in a block heater (Stuart SBH130D) for different predetermined times.

EXTRUSION

The extrusion was performed with a co-rotating twin-screw-extruder Werner & Pfleiderer ZSK 25 at different temperatures and humidity conditions in a continuous process. The extrusion of wet leather shavings resulted in samples with granular appearance, on the other hand the dry shavings gave rise to a powder sample.

HYDROTHERMAL TREATMENT

Leather shavings were subjected to hydrothermal treatment through a continuous autoclave system attached to a refiner (ANDRITZ) at different temperature and pressure conditions.

ASSESSMENT OF THE PRE-TREATED SAMPLES

DIFFERENTIAL SCANNING CALORIMETER (DSC)

Thermal profiles of the pre-treated samples were taken from 0 to 130°C using DSC (DSC 1 STARe System Mettler Toledo) to assess thermal changes as a function of input temperature. The pH was previously adjusted to 7 washing the samples with KH_2PO_4/K_2HPO_4 buffer solution. DSC results determine the enthalpy of the denaturation process i.e., the energy necessary to break down the hydrogen bridges that stabilize the triple helix.

DEGRADATION BY TRYPSIN

The denaturation degree was measured with the protease trypsin. Leather shavings were placed in safe-lock microcentrifuge tubes with NH_4HCO_3 solution and left overnight, then trypsin solution was added at 37 °C during 5 hours and washed out with distilled water. Degradation by trypsin measures the capacity of trypsin to digest the samples also taking in consideration the breakdown of covalent bonds between carbon atoms.

BIOGAS PRODUCTION

Anaerobic digestion experiments were performed under mesophilic conditions (37 °C ± 2 °C) according to VDI 4630 (2006) in triplicate. Tests were conducted using 65 ml reactor flasks in a shaker water bath. The gas production was monitored on a daily basis with a digital manometer (Leo 3 Keller). The mesophilic anaerobic inoculum was anaerobic sludge from the local sewage treatment plant. Biogas production is given in norm liters (273 K and 1013 hPa) per kg of organic dry matter ($l_N.kg_{oDM}$).

RESULTS

Based on analysis of DSC and degradation by trypsin results it is possible to conclude that the pre-treatments accomplished to degrade the collagenous structure of the samples. In all cases the degradation by trypsin is more sensitive to evaluate the susceptibility of the pre-treated samples to enzymatic degradation.

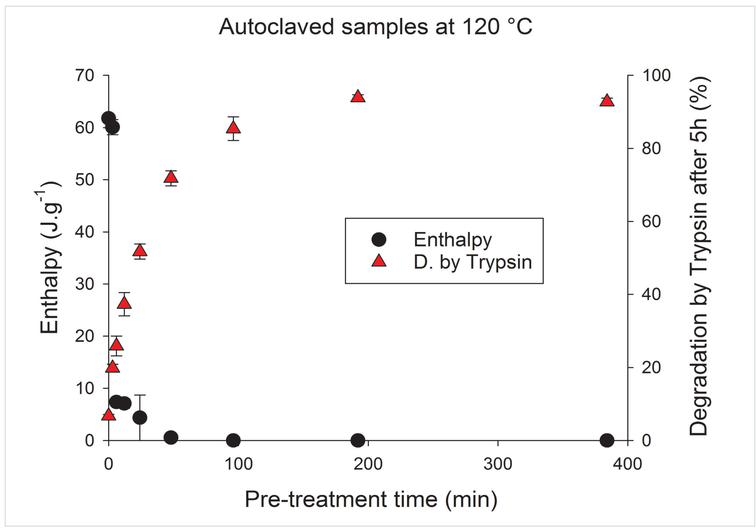

Fig. 1: Comparison of DSC with degradation by trypsin for the autoclaved samples regarding the autoclaving time.

The untreated leather shavings showed almost 7% degradation after treatment with trypsin. Autoclaved samples showed a degradation degree of 50% with only 24 min of pre-treatment and it was possible to reach more than 90% after 192 minutes (Figure 1). The extruded samples that were moistened before the pre-treatment obtained higher degradation levels. It was possible to reach 35% of degradation by trypsin with the highest tested temperature (Figure 2.a). The hydrothermally treated samples showed a linear growth trend with the temperature and the sample pre-treated at 170°C reached a degradation by trypsin of 90% (Figure 2.b).

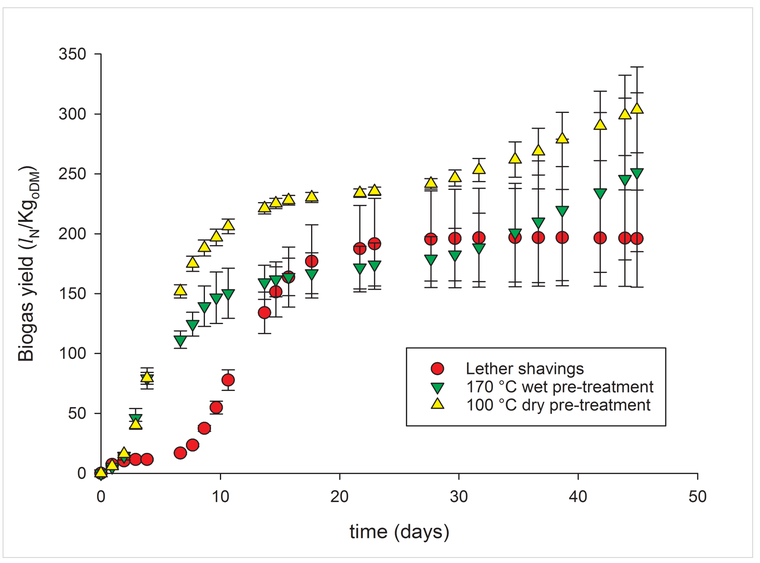

Fig. 3: Biogas generation profiles for the degradation of the untreated sample and extruded samples.

Results showed that pre-treated samples start to produce biogas approximately five days before the untreated sample. Moreover after a stagnation time the extruded samples start to produce again while the leather shavings remain stagnated and it is possible to see that more time is necessary to evaluate this samples. Although the sample treated at 100 °C was less degraded by trypsin than the sample treated at 170 °C, this sample showed higher biogas yield. A reason can be, that this sample is a powder like material favoring contact with the inoculum and anaerobic bacteria

CONCLUSIONS

- The pre-treatments increase the degradability of leather shavings
- Decrease the onset time of biogas production in 5 day was possible
- Longer times are needed to reach the whole biogas production capacity of the extruded samples

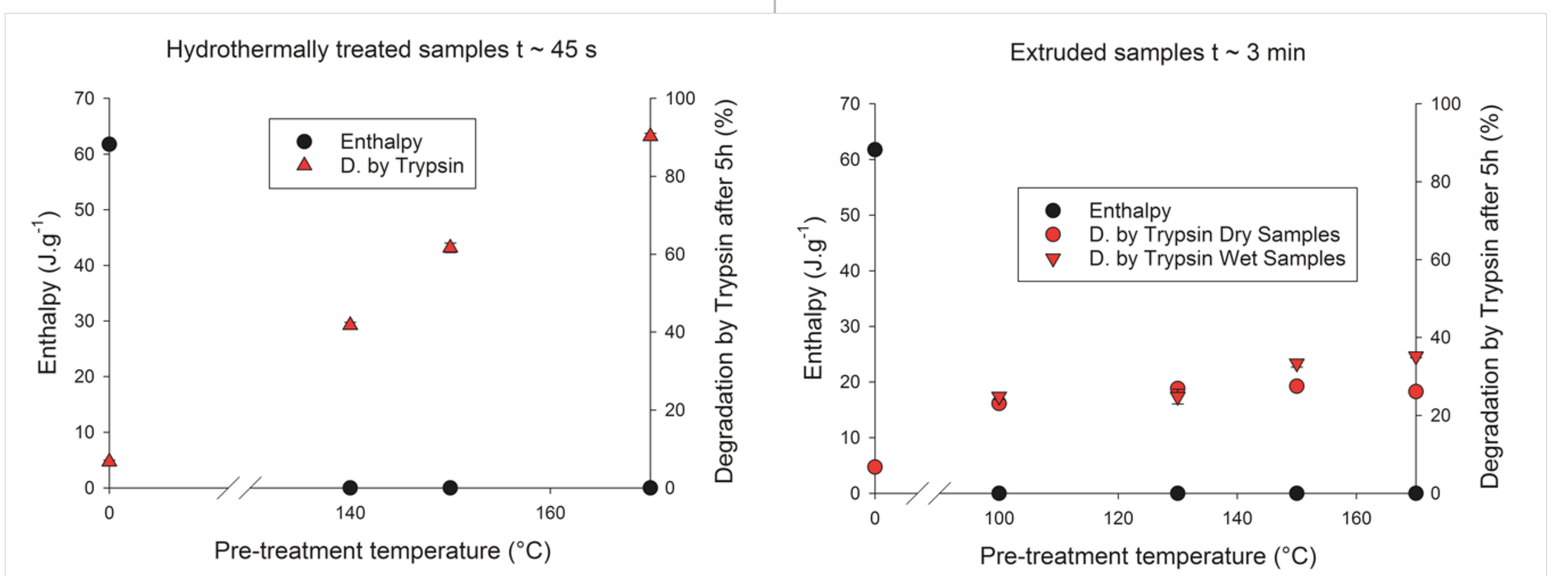

Fig. 2: Comparison of DSC with degradation by trypsin for the extruded samples (a) and hydrothermally treated samples (b) regarding the pre-treatment temperature.

Two of the extruded samples (treated dry at 100 °C and wet at 170 °C) and the untreated leather shavings were tested for biogas production (Figure 3).

CONTACT
Carolina Scaraffuni Gomes
Telefon+49 3731 366-228
Email: carolina.scaraffunigomes@filkfreiberg.de
Forschungsinstitut für Leder und
Kunststoffbahnen (FILK) gGmbH
Meißner Ring 1-5
09599 Freiberg / Deutschland
www.filkfreiberg.de

PARTNER:
[1]Forschungsinstitut für Leder und
Kunststoffbahnen (FILK) gGmbH
[2]TU Bergakademie Freiberg, Institut für Thermische Verfahrenstechnik,
Umwelttechnik und Naturstoffverarbeitung

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