Supporting information for

A 'Trojan Horse Strategy' for the development of a renewable leather tanning agent produced via an AlCl₃-catalyzed cellulose depolymerization

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Experimental

Materials

Microcrystalline cellulose, $AlCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3$ and NaCl were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China), and the reagents used for analysis were of analytical grade. Pickled cattle pelt was purchased from Haining Ruixing Leather Co., Ltd, and the chemicals used for leather processing were of industrial grade.

Preparation of Al-oligosaccharides tanning agent

Microcrystalline cellulose and $AlCl_3 \cdot 6H_2O$ were mixed directly with deionized water in four microwave Teflon tubes. The reaction tubes were subsequently heated using an Anton Paar microwave reactor with continuous stirring. Temperature was monitored inside the reaction tube using a Ruby probe. Each reaction was heated from room temperature to the designed temperature within 10 min, and held for differing periods. After treatment, the reaction system was cooled down to a temperature below 50 °C using compressed air. The post-treatment slurry was filtered to separate the solid residue from the liquid fraction. The collected solid residue was dried overnight in an oven at 105 °C to calculate the overall conversion. 15 wt% of NaCl were added for the extraction of small molecular weight products, using a 20 vol% THF solution as extraction layer for three times. After extraction, the residual THF solvent in the tanning agent was removed by rotary evaporation at 40 °C for 1 h.

Characterization of liquid products in the tanning agent

The monomeric products were quantitatively measured by high-performance liquid chromatography (HPLC, Waters) with RI and UV detectors.

The molecular weight distribution of the oligomers in the H_2O phase before and after extraction was analyzed using gel permeation chromatography (GPC, Agilent 1260) with a PL aquagel-OH column (Agilent) and a RI detector, and ultrapure water was used as the mobile phase at a flow rate of 1.0 mL/min.

Tanning process

Pickled cattle pelt was tailored along the back bone into matched pieces. Then they were tanned with the obtained tanning agent at 1:1 weight ratio based on the weight of pickled pelt in the drum. After running for 4 h, the pH of the tanning liquor was progressively adjusted to *ca.* 4.0 with a sodium bicarbonate solution at an interval of 10 min. The drum kept running for 4 h at 40 °C and then stood for 12 h to achieve a complete crosslinking reaction between tanning agent and collagen fiber. The resultant tanned leather was finally washed with water at room temperature for 1 min, and then dried with air for further evaluation.

Chemical and physical testing of the tanned leather and the post tanning agent

The shrinkage temperature (T_s) of the tanned leather was measured and recorded using a digital leather shrinkage temperature instrument (MSW-YD4, Shanxi University of Science and Technology, China). The rate of heating was kept at 2

^{o}C/min. Each sample was tested for two times.

After the freeze drying step, to remove the moisture of leather, the cross section of the tanned leather was observed using scanning electron microscope (SEM, JSM-7500F, JEOL, Japan) equipped with energy-dispersive spectrometry (EDS) analysis.

The grain surface of the tanned leather was observed using a stereo-microscope (SZX12, Olympus, Japan).

Color measurement parameters (L, a, b) of the tanned leather were recorded using a color measurement instrument (Color reader CR-13, Konica Minolt, Japan). The total color difference (ΔE) was calculated based on a standard white card. The color difference of the tanned leather was recorded from 8 different positions.

Analysis of the rest aluminium and organic components in the post tanning agent

After tanning, the wastewater were collected and the residual aluminium and TOC concentrations were quantitatively measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 8000DV, PerkinElmer, USA) and a TOC Analyzer (TOC, vario, Elementar, Germany), respectively. The TOC and ICP analyses were conducted in triplicate.

Computational Details

Full geometry optimizations in the aqueous solution were performed to locate all the stationary points, using the PBE0 method,[1] with the 6-311+G(d, p) basis set for C, H, O, and N atoms,[2] and the aug-cc-pvtz basis set for Al atoms,[3] namely PBE0/6-311+G(d, p), aug-cc-pvtz. Furthermore, the PBE0/6-311+G(d, p), aug-cc-pvtz theoretical level has been successfully applied to the analogous reaction system.[4] Unless otherwise specified, the Gibbs free energy of formation (ΔG) is relative to the initial reactants including the ZPE correction obtained at the PBE0/6-311+G(d, p), aug-cc-pvtz level. All geometry calculations were run with the Gaussian 09 program.[5] Atomic charges were analyzed by the natural bond orbital (NBO) method.[6] To gain a deeper insight into the electronic properties, the activity index analysis (electrophilicity index ω and nucleophilicity index N) of the reactants was performed.[7] Meanwhile, local electrophilicity ω_{κ} and local nucleophilicity N_{κ} indices are defined as $\omega_{\kappa} = \omega P_{\kappa}^{+}$ and $N_{\kappa} = N P_{\kappa}^{-}$ atom κ electrophilic and nucleophilic Parr functions (P_{κ}^{+} and P_{κ}^{-}) are originated from the Mulliken atomic spin density analysis at the radical cation and at the radical anion of the corresponding reagent, respectively.[8]

References
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Reaction temperature

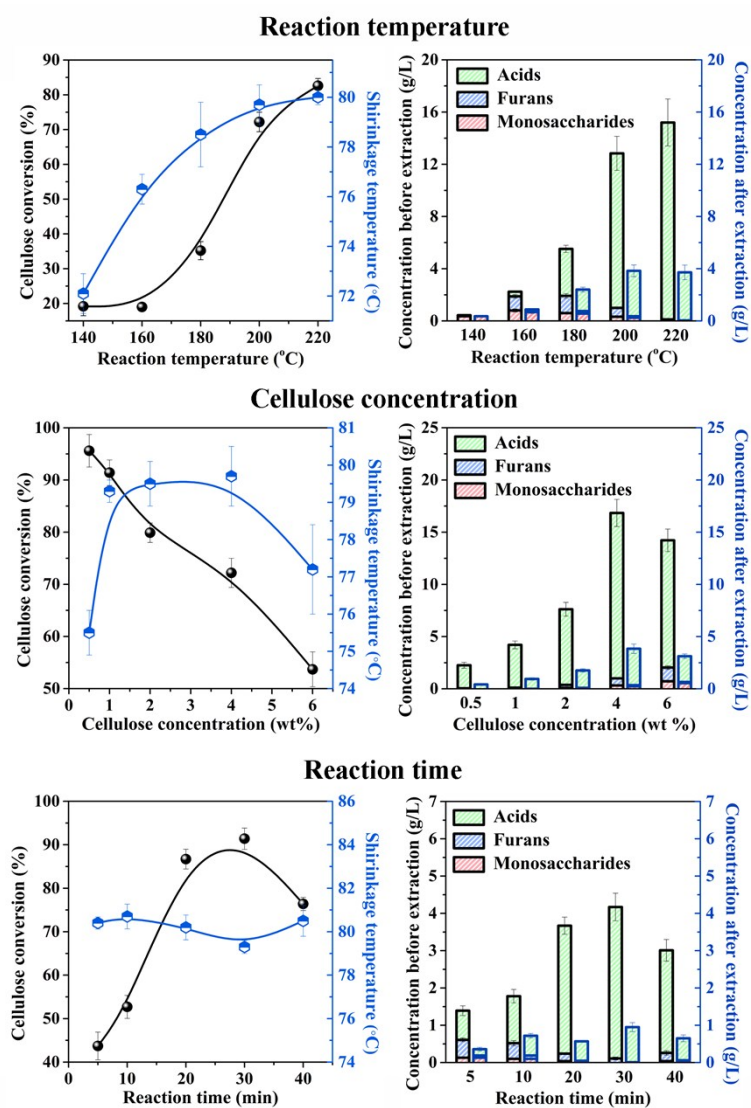**Cellulose concentration**

Reaction time

Fig. S1 Effect of reaction temperature, cellulose concentration and reaction time on the conversion of cellulose and shrinkage temperature of the leather tanned by the reaction fluids and on the dispersion of small molecule products.
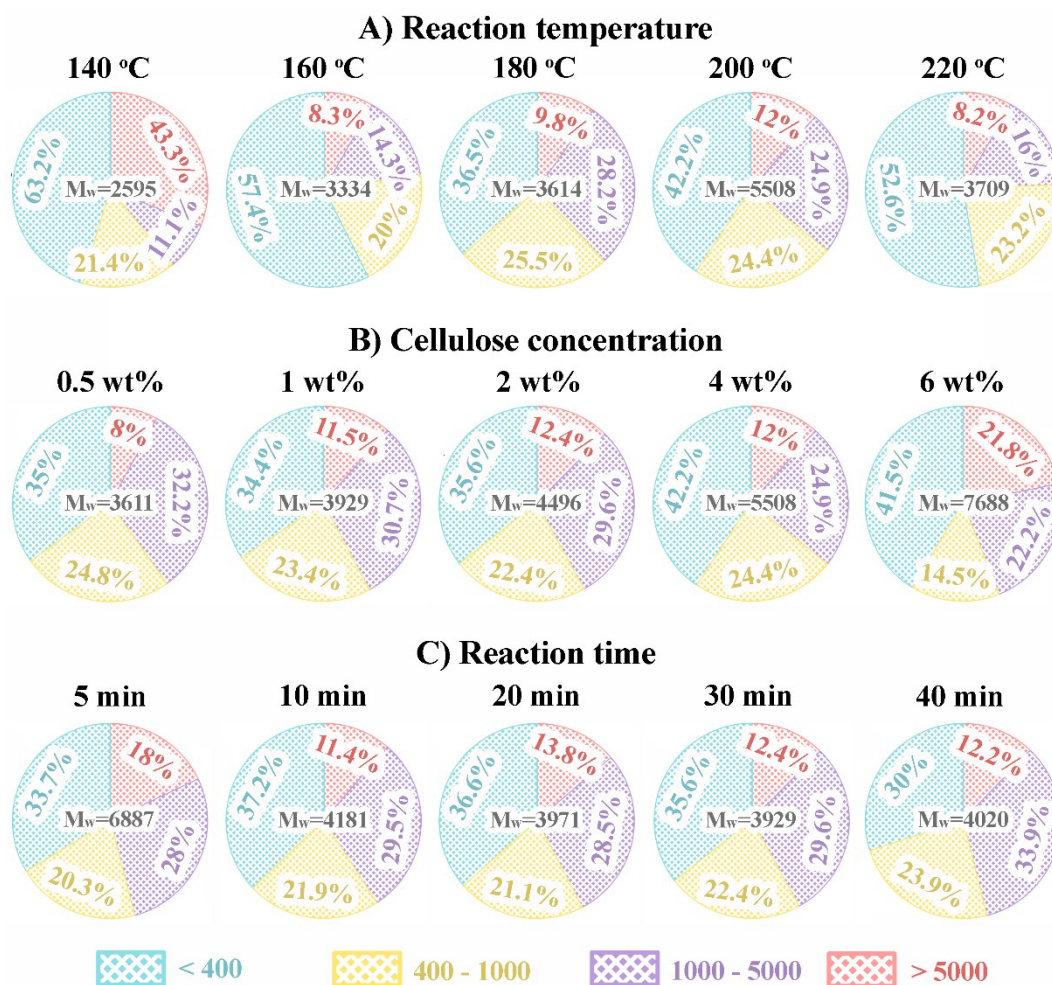
Fig. S2 Molecular weight distribution of the oligomers (after extraction) from cellulose conversion using different reaction temperature, cellulose concentration and reaction time.
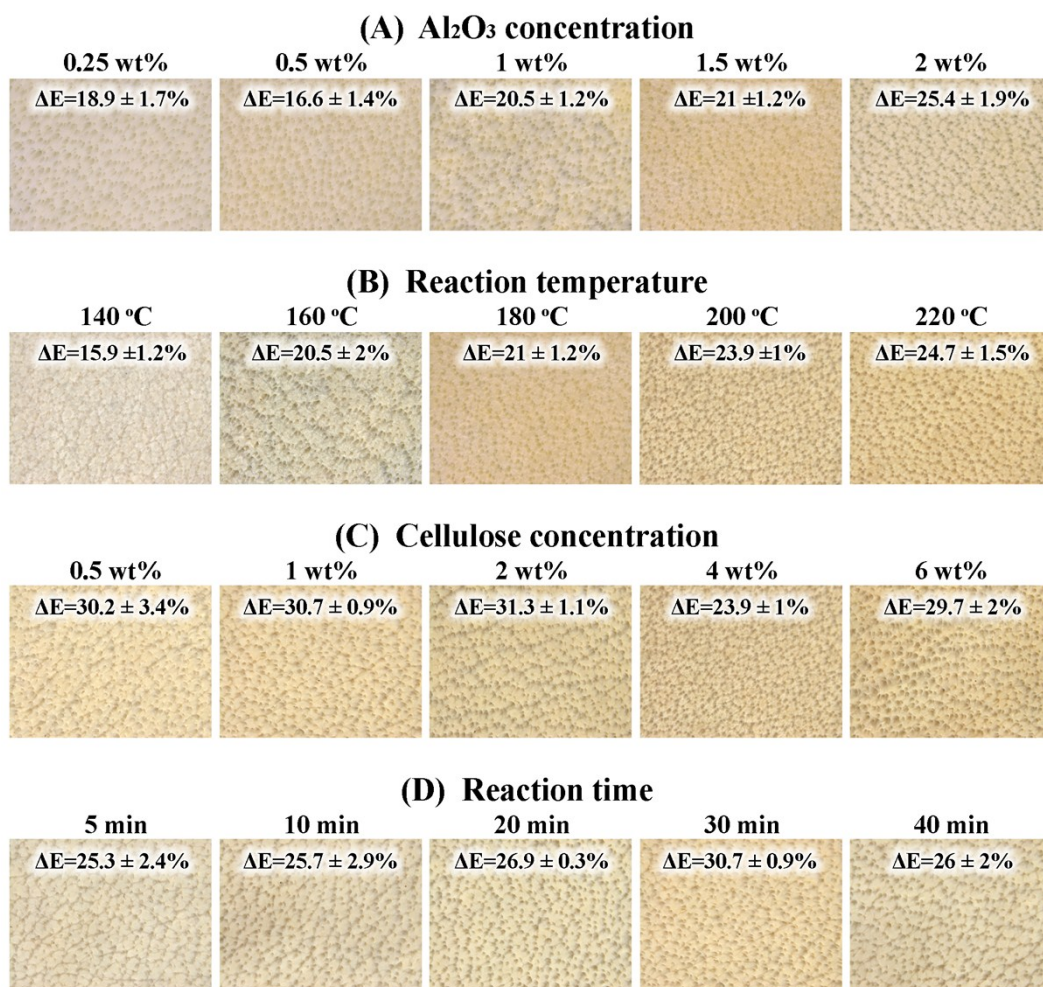
(A) Al₂O₃ concentration

0.25 wt%	0.5 wt%	1 wt%	1.5 wt%	2 wt%
ΔE=18.9 ± 1.7%	ΔE=16.6 ± 1.4%	ΔE=20.5 ± 1.2%	ΔE=21 ±1.2%	ΔE=25.4 ± 1.9%

(B) Reaction temperature

140 °C	160 °C	180 °C	200 °C	220 °C
ΔE=15.9 ±1.2%	ΔE=20.5 ± 2%	ΔE=21 ± 1.2%	ΔE=23.9 ±1%	ΔE=24.7 ± 1.5%

(C) Cellulose concentration

0.5 wt%	1 wt%	2 wt%	4 wt%	6 wt%
ΔE=30.2 ± 3.4%	ΔE=30.7 ± 0.9%	ΔE=31.3 ± 1.1%	ΔE=23.9 ± 1%	ΔE=29.7 ± 2%

(D) Reaction time

5 min	10 min	20 min	30 min	40 min
ΔE=25.3 ± 2.4%	ΔE=25.7 ± 2.9%	ΔE=26.9 ± 0.3%	ΔE=30.7 ± 0.9%	ΔE=26 ± 2%

Fig. S3 Grain fitness and whiteness (ΔE) of leather tanned by the reaction fluids with different (A) Al_2O_3 concentration, (B) reaction temperature, (C) cellulose concentration and (D) reaction time.

Table S1 Al adsorption, carbon absorption and thickening ratio of leather tanned by the reaction fluids with different Al_2O_3 concentration and cellulose concentration.

Samples		Al absorption (wt%)	Carbon absorption (wt%)	Thickening ratio (%)
Al_2O_3 concentration (wt%)	0.25	82.2 ± 1.5	1.5 ± 0.2	37.1 ± 2.6
	0.5	84.0 ± 1.1	15.8 ± 0.7	49.4 ± 2.9
	1	88.6 ± 0.6	19.5 ± 1.2	49.2 ± 2.1
	1.5	90.1 ± 1.8	32.7 ± 1.1	54.0 ± 3.5
	2	98.0 ± 0.5	38.3 ± 1.9	76.8 ± 2.7
Cellulose concentration (wt%)	0.5	83.4 ± 1.2	30.8 ± 1.5	47.0 ± 3.2
	1	87.5 ± 0.8	33.9 ± 1.1	39.2 ± 2.4
	2	85.5 ± 0.2	39.2 ± 0.5	38.2 ± 1.5
	4	93.7 ± 0.6	59.0 ± 0.2	56.0 ± 3.7
	6	79 ± 1.7	19.8 ± 0.4	43.5 ± 1.8