

## Optimising chemo-enzymatic separation of polyester cellulose blends

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### ABSTRACT

The study demonstrates the potential of enzymatic hydrolysis and alkaline pretreatment for sustainable blended textile recycling. The target is complete cellulose removal while preserving the polyester integrity for recovery. Interactions of sodium hydroxide concentration (10 %–30 %), urea concentration (0 %–12 %), and temperature (-20 °C–50 °C) were investigated during pretreatment using a design of experiments. Analysis revealed a bimodal pattern in polyester mass loss, with one peak at lower concentrations and temperatures, and a more prominent peak at higher concentrations and temperatures. Cellulose hydrolysis also occurred under high NaOH concentrations and elevated temperatures (50 °C, 30 % NaOH, 0 % urea). Optimal conditions, preserving polyester integrity while achieving complete cellulose elimination, were identified at temperatures between 6.2 °C and 13.3 °C, with NaOH concentrations of 20.7 %–26.6 % (0 % urea) or 13.9 % NaOH and 12 % urea. These findings pave the way for a greener, more efficient textile recycling, advancing the circularity for textiles.

### 1. Introduction

Production and consumption of textiles has increased exponentially in the last two decades on a global scale. In particular, fast fashion business models fuel the consumption of textiles. The sector turned over 91 bn€ in 2021, and it is estimated that sales will more than double by 2027, reaching 185 bn€ (Smith, 2023). Rising sales coupled with falling prices for textiles have inevitably led to an increased demand for fibres. This peaked at 113·10<sup>6</sup> t in 2021 when nearly double the amount of the second most important industrial metal, aluminium, at 67.5·10<sup>6</sup> t (Textile Exchange, 2020; U.S. Geological Survey, 2023) was needed. Textiles have even entered the top 10 sources of waste alongside food, paper, plastic, and glass-derived materials and have, therefore, been identified as an upcoming source of crisis especially in the third world (Dissanayake and Weerasinghe, 2021; Vera et al., 2022). Due to the lack of regulated waste management strategies, textile waste is mostly incinerated or landfilled, resulting in fundamental environmental and

social risks. To mitigate these dangers, a reconsideration of how to handle *end-of-use* textiles is required (Jamshaid et al., 2021; Dissanayake et al., 2021). Campaigns to reduce textile waste have been launched in collaboration of policy, industry, and academia.

In the European Union, textile waste has not been an issue until recently. In 2015, the Commission launched the EU action plan for Circular Economy (EC, 2015), with no specific focus on textiles within the document. It was not until the amendment of the Waste Framework Directive (WFD) in 2018 (EC, 2018) that textiles came into the Commission's attention. Subsequently, further documents were published by the Commission to regulate the handling of textiles and textile waste. Important to mention are the Circular Economy Action Plan in 2020 (EC, 2020), the EU Strategy for Textiles in 2021 (EC, 2021), the EU Strategy for Sustainable and Circular Textiles in 2022 (EC, 2022) and a proposal for an amendment of the WFD (EC, 2023). Although the Commission has not yet set specific quotas for the collection and recycling of textiles, for example, Member States must organize separate

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collection and implement an EPR system for textile waste from 2025 onwards (European Commission, 2015, 2018, 2020, 2021, 2022, 2023).

To fulfil favorable properties, textiles commonly consist of two or more polymers such as cellulose and polyester or more precise polyethylene terephthalate. This fact complicates the technical implementation of recyclability whereas fibre recycling of unblended natural and synthetic fibres is already possible and done (Kahoush and Kadi, 2022). In addition to traditional chemical and mechanical recycling methods, bio-based approaches including composting, anaerobic digestion, and biocatalytic depolymerization have been developed as alternative routes for textile recycling (Ribul et al., 2021). Biocatalysis, which is executed by enzymes, has gained particular industrial relevance, as it works under mild reaction conditions, exhibits high activity and acts specifically as catalysts of diverse chemical reactions (Cipolatti et al., 2019). In terms of textile recycling, biocatalysis offers a powerful and environmentally friendly tool to selectively provide valuable building blocks and monomers (Pellis et al., 2018).

Cellulases are enzyme systems capable of degrading cellulose to glucose. Their ability to degrade cellulosic waste has first been reported in 1974 by Mandels et al. with a conversion rate of 92 % (Mandels et al., 1974). Commercially available cellulases consist of synergistically working individual enzymes including e.g. endoglucanases, cellobiohydrolases beta-glucosidase and polysaccharide monoxygenases (Quartinello et al., 2018). Their comparable low price makes them industrially applicable for cellulosic fibre processing (Piribauer and Bartl, 2019).

However, crystalline regions of cellulose lead to an inherently high resistance to chemical and biological depolymerisation (Chandawat et al., 2011). This fact can be circumvented by a pretreatment, e.g. with NaOH, a process which is also reported as mercerization. Details of this morphological transformation are further described in literature (Pérez and Samain, 2010; Chandawat et al., 2011; Ferro et al., 2020; Popescu 2017). NaOH treatment of cellulose initiates the stepwise transformation from crystalline cellulose I to alkali cellulose and further to a new allomorph termed cellulose II which is more accessible to enzymes (Pérez and Samain 2010; Sayyed et al., 2019). The process of treating cellulose with NaOH is generally divided into four morphological levels that depend mainly on concentration and temperature. At low NaOH concentrations, cellulose starts swelling - visible in form of an expansion in size. Increasing NaOH concentration leads to dissociation of hydrogen bonds, enhancing accessibility of hydroxyl groups. Mercerization occurs after a further increase in concentration and includes the transformation from cellulose I to cellulose II, which is favorable for enzymatic depolymerisation (Mansikkamäki et al., 2005). Degradation of cellulose starts at NaOH concentrations > 15 % (w/v). Complete mercerization of native cellulose has been reported at concentrations between 7 % (w/v) and 15 % (w/v) (Duchemin, 2015; Oudiani et al., 2011). However, NaOH pretreatment with concentrations > 16 % (w/w) lead to the highest saccharification rates (Ling et al., 2017; Piribauer et al., 2021).

Previous studies have demonstrated that the impact of mercerization can be amplified by the addition of urea although the precise mechanism behind this phenomenon is unknown (Gupta et al., 2013; Mohsenzadeh et al., 2012; Gholamzad et al., 2014; Jones and Brischke, 2017; Li et al., 2019; Cai and Zhang, 2005).

Temperature also plays a crucial role. Ferro et al. investigated crystallinity and structural conversion rate of cellulose at diverse temperatures and proved that higher temperatures enhance the transformation from crystalline cellulose I to amorphous cellulose II, whereas others demonstrated, that lower temperatures in combination with urea lead to an enhanced transformation (Zhao et al., 2008; Dai et al., 2015; Williams et al., 2011; Ferro et al., 2020).

At temperatures above the glass transition temperature carbonyl groups of polyester are also attacked by NaOH. Low molecular chains are removed due to the formation of hydroxyl and carboxyl end groups on the fibre surface. This attack is caused by electron deficiency of the acid carbonyl, which results in a molar mass decrease of the polymer and

additionally a reduction of the tensile properties of the fibre. Degradation of polyester can be amplified by higher NaOH concentrations and longer treatment times (Kish and Nouri, 1999; Ellison et al., 1982; Musale and Shukla, 2017). According to previous studies, there is no evidence that urea has an impact on the degradation of polyester.

NaOH pretreatment of cellulose prior to enzymatic hydrolysis has been reported as an effective biorefinery process step to overcome high crystallinity by several groups (Jeihanipour and Taherzadeh 2009; Gholamzad et al., 2014; Piribauer et al., 2021; Lehto and Alén 2015; Boondaeng et al., 2023). However, when this process is applied to recover polyester fibres from blends with cellulose, concomitant degradation of polyester must be avoided/minimized. In terms of optimal conditions such as concentration of NaOH and urea and temperature, there seems to be a sophisticated interplay between the individual factors. Therefore, a design of experiment study (DoE) was conducted to gain more information on optimal conditions for pretreatment and to obtain an economically viable process. In a first step, treatment of pure polyester and pure cotton textiles was investigated and models predicting mass loss as function of NaOH concentration, urea concentration and temperature were developed. Insights acquired from these models were subsequently considered for the design of the process for blended textiles.

## 2. Materials and methods

### 2.1. Materials

Pure cotton textiles were provided by Lenzing AG (Lenzing, Austria) and pure polyester textiles by Linz Textil GmbH (Linz, Austria). Blended textiles (65 % polyester, 35 % cotton) were purchased from a regional retailer (Kik, Bönen, Germany) and washed once. All textiles were milled using a cutting mill (MAS1, Wittmann Battenfeld GmbH, Kottlingbrunn, Austria) equipped with a screen with 4 mm sized round holes and a cyclone for collection. Samples are presented in Fig. 1 as they were employed for the experiments. The cellulase cocktail (NS 59,150) was kindly provided by Novozymes A/S (Bagsværd, Denmark). NaOH was purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany). All other chemicals were purchased from Sigma-Aldrich (Merck KGaA (formerly Sigma-Aldrich), Darmstadt, Germany) and used without further purification, if not stated otherwise.

### 2.2. Pretreatment of textiles

#### 2.2.1. Pretreatment methods for enzymatic cellulose hydrolysis

To identify the most appropriate pretreatment, selected chemical and physical methods were applied to pure cotton textiles. Specifically, NaOH treatment with 12 % (w/w) at -20 °C (Gholamzad et al., 2014), trifluoroacetic acid (TFA) treatment (Zhang et al., 2018), steam explosion (Stex) at 140 °C with a holding time of 2 min and electron beam irradiation (EBI) at a dosage of 75 kGy were examined with uncut textiles. Further a shredder (Shred) was used to cut the textile to 4 mm without any further treatment.

#### 2.2.2. Pretreatment with NaOH investigated using DoE

NaOH/urea-solutions were prepared with deionized water and pretreated at least for 16 h. For each experiment, 4 g of textile substrate was weighed in a beaker. Pretreatment was conducted with 400 mL NaOH/Urea-solution to have 1 % (w/v) solid load. Suspensions were mixed until homogeneity using a glass stick and incubated at respective temperatures with occasional stirring for 40 min. Washing until neutral pH was performed using a sieve with mesh width of 0.10 mm (Riffert, Eferding, Austria). Samples were used for hydrolysis without any further drying step. Temperature treatment at -20 °C was implemented in a freezer (Liebherr, Bulle, Switzerland). Experiments at 21 °C (room temperature) were kept on the bench. Incubation at 50 °C was performed in a heating incubator (Bühler, Uzwil, Switzerland).

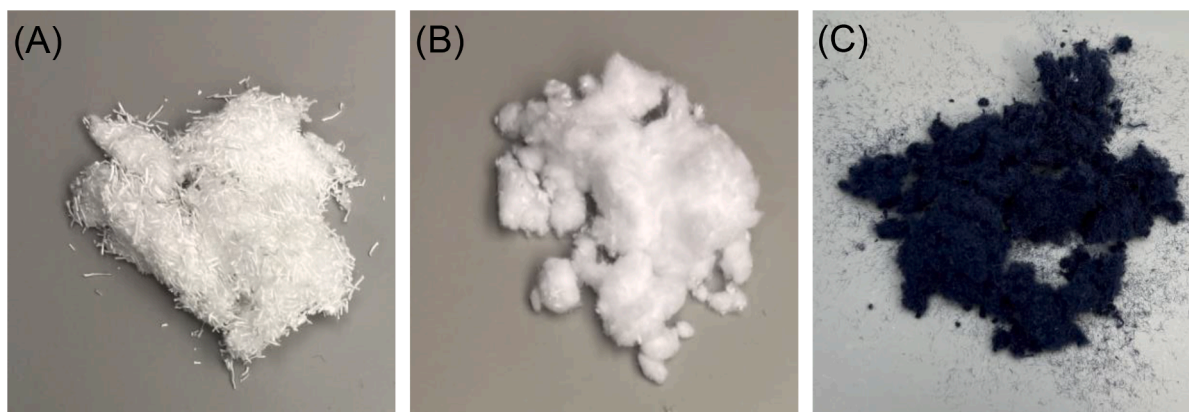


Fig. 1. Samples after shredding and before treatment – polyester (A), cellulose (B), blended textile (C).

Temperature within the solution was monitored constantly.

### 2.3. Enzyme and hydrolysis characteristics

Hydrolysis conditions were consistently the same for all experiments: Experiments were performed in 1-L-Schott-flasks and 50 mM citric acid buffer at pH 5.0 with sodium azide (0.02 %) to prevent contamination. The textile substrate was applied with a solid load of 0.8 % (w/v) in 500 mL buffer. Enzyme dosage was set to an activity of 0.68 filter paper units (FPU) per g cellulose, determined according to Adney and Baker (2008). Hydrolysis was performed at 50 °C and 70 rpm orbital shaking for 24 h in a heating incubator (Bühler, Uzwil, Switzerland).

Complete hydrolysis was conducted following the methodology outlined above, but hydrolysis time was extended to 96 h. To mitigate effects of product inhibition of cellulases, 100 mL hydrolysate was refreshed with a fresh enzyme-buffer solution every 20 h, and sampling was conducted both before and after each exchange (Hsieh et al., 2014).

### 2.4. Design of experiments (DoE)

Statistical analyses and modelling were carried out using Design-Expert® Software Version 10 (Stat-Ease, Minneapolis, Minnesota, United States). A full factorial central composite design (3 factors and 3 levels) was conducted. The selection of factors and the determination of their levels were based on previous studies and a preliminary internal design of experiments that investigated the influence of urea and different temperatures on the NaOH pretreatment of blended textiles. Moderate temperatures were especially selected in terms of economic implementation of the process. All factors including their respective levels are provided in Table 1. The centre point was repeated 8 times. Different designs were applied, where mass loss and glucose yield were defined as responses (Table 2). Data analysis was performed using Analysis of Variance (ANOVA) to determine significance with  $p$ -value < 0.05, and the response surface method was applied to model interactions of the investigated levels. Temperature was monitored for all experiments and actual temperatures of the solutions, which slightly differed to the theoretical temperature, were used within the software.

Due to variations in theoretical and actual temperature, mass losses of design 1 and design 3 (Table 2) could not be directly combined into the same design. To address this issue, the mass losses for cellulose were

Table 1

Factors and levels used for experiments to statistically model NaOH/urea pretreatment.

Factor	Level 1	Level 2	Level 3
NaOH concentration [%]	10	20	30
Urea concentration [%]	0	6	12
Temperature [ °C]	−20	21	50

Table 2

Overview on design studies.

Design	Substrate	Response 1	Response 2
1	polyester	mass loss after pretreatment	–
2	cellulose	mass loss after pretreatment	–
3	cellulose	mass loss after pretreatment and hydrolysis	glucose yield 24 h

harmonized to the same temperatures used for polyester through numerical optimization tool specific to the corresponding model. This approach led to the creation of an additional calculated design.

### 2.5. Analytics

Solid residues after pretreatment were washed and dried for 24 h at 50 °C in an oven (E28, Binder GmbH, Tuttlingen, Germany). Solid residues, after pretreatment and a certain time of hydrolysis, were vacuum filtered through a 90 mm paper filter (Macherey-Nagel, Düren, Germany) and dried similarly. Mass loss was calculated according to Eq. (1) where  $m_1$  and  $m_2$  are the masses before respectively after the treatment:

$$\text{mass loss} = \left(1 - \frac{m_1 - m_2}{m_2}\right) \cdot 100\%. \quad (1)$$

Filters were uniformly dried and weighed in advance, and the mass of the filter was subtracted from the final mass.

Assessment of glucose yield was performed using a HPLC system (UFLC, Shimadzu, Kyoto, Japan) equipped with HyperREZ™ XP Carbohydrate  $H + 300 \times 7.7$  mm column (ThermoScientific, Waltham, Massachusetts, United States) and RID detector. Measurements were run with 5 mM  $H_2SO_4$  at a flow rate of 0.6 mL/min and 65 °C. Glucose yield was determined according to Eq. (2), where  $m_{Glucose}$  is the amount of produced glucose and  $m_{Cellulose}$  is the amount of cellulose added to the reaction at the beginning (related to the cellulose content of the blended textile):

$$\text{Glucose yield} = \frac{m_{Glucose}}{m_{Cellulose} \cdot 1,11} \cdot 100\%. \quad (2)$$

The initial amount of glucose already present in the enzyme cocktail was subtracted from all measurements. Glucose could not be detected in spent NaOH/urea solution and was, therefore, not included in the calculations.

Molecular weight of cellulosic samples was determined as previously described Schelosky et al. (1999) using size exclusion chromatography (Agilent PLgel-mixed 20  $\mu$ m, 7.5  $\times$  300 mm, Santa Clara, United States) coupled with a Bio-Inert 1260 Infinity II pump and an autosampler. Detection was performed using a Wyatt Dawn DSP MALS detector with an argon ion laser ( $\lambda_0 = 488$  nm), a Spectra System TSP FL 3000 fluorescence detector at 290 nm excitation and 340 nm emission, and a

Shodex RI-71 refractive index detector. The system was set to a flow rate of 1.00 mL min<sup>-1</sup> with 0.9% N,N-dimethylacetamide/LiCl (DMAc/LiCl), where 100 µL sample were injected with a run time of 45 min. Data analysis was executed using Astra 4.7, GRAMS/AI 7.0, and OriginPro 2019. The only notable deviation from the protocol was that the mass of sample was reduced by 90 %, resulting in a reduced viscosity of the DMAc/LiCl solutions. The polydispersity index was calculated as previously described (Friebel et al., 2019).

A High performance anion exchange chromatography (HPAEC) system (Dionex ICS-5000+, ThermoScientific, Waltham, Massachusetts, United States) was used to detect released glucose in NaOH/urea-solutions. The system consisted of the pre-column CarboPac PA20 3 × 30 mm and the main-column CarboPac PA20 3 × 150 mm. The column temperature was 30 °C with 1.5 mM NaOH as eluent at a flow rate of 0.5 mL min<sup>-1</sup>. Before each measurement, the columns were flushed with 200 mM NaOH. Detection was performed by a Pulsed Amperometric Detector.

Hydroxycarboxylic acids can only be determined in NaOH-solutions without urea. NaOH-solutions were titrated to neutral pH with sulfuric acid and lyophilized (Martin Christ Gefriertrocknungsanlagen GmbH, ALPHA 1–2 LDplus, Osterode am Harz, Germany). The salts were mixed with 900 µL anhydrous pyridine (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and heated to 70 °C (E28, Binder GmbH, Tuttlingen, Germany) for 1 h. Derivatization was initialized by the addition of 100 µL BSTFA at 70 °C for 1 h. Analyses were conducted using a gas chromatography system (QP2010, Shimadzu, Kyoto, Japan), equipped with an HP5-MS column (60 m length × 0.25 mm inner diameter × 0.25 µm film thickness) and QP2020 dual stage mass spectrometer. Measurement and data analysis was performed as described previously (Schlack et al., 2021).

The intrinsic viscosity (IV) was measured in accordance with the ISO standard 1628–5. Solutions of 0.5 % (m/v) of the polyester were prepared in a 1:1 mixture of phenol (VWR International, LLC, Radnor, Pennsylvania, United States) and (1,2)-dichlorobenzene (Merck KGaA, Darmstadt, Germany). Viscosity measurements were performed using an Ubbelohde capillary viscosimeter (AVS 370, Xylem Analytics, Weilheim, Germany) situated in an oil thermostat bath set to 25.0 °C. All measurements were performed in duplicate and the IV value was determined using the Billmeyer calculation method.

For the crystallinity index determination, the samples were measured with the S-Max 3000 (Rigaku Corporation, Tokyo, Japan) with MM002+ X-ray source (Cu-Kα, λ = 0.1542 nm) and the FUJI Image Plate, a two-dimensional X-ray sensitive film. The samples were put between polymer film for support and measured in vacuum for 3600 s. 2D-XRD, respectively Wide-angle X-ray diffraction images, were acquired, integrated, calibrated and background corrected. Related polyester peaks between 2θ = 16–35° in the resulting scattering curves were fitted with gaussian functions and additional gaussian background in order to identify the peak areas related to crystalline regions A<sub>c</sub> and the area related to amorphous regions A<sub>a</sub>. Crystallinity index X<sub>c</sub> was calculated according to Eq. (3):

$$X_c = \frac{A_c}{A_c + A_a} \quad (3)$$

The polyester content was determined by differential scanning calorimetry (DSC) with TA Q20 (Waters Milford, Massachusetts, United States). Measurements were carried out under nitrogen (50 mL min<sup>-1</sup>) from –40 °C to 270 °C, using a heating rate of 10 K min<sup>-1</sup>. The method was established by measuring 30 calibration samples and plotting the melting enthalpy against the known polyester content. Melting enthalpy was thereby calculated by TA Instruments Universal Analysis 2000

Version 4.5A (New Castle, Delaware, United States).

Structural carbohydrates within the fibres were determined according to the NREL method NREL/TP-510-42618. The sample mass was reduced to 150 mg fibres. Monosaccharides were quantified by HPAEC as for the determination of glucose in NaOH/urea-solution. Acid soluble lignin was not determined in this case (Sluiter et al., 2008).

Fourier transformed infrared spectroscopy (FTIR) was conducted using an IR-Spectrometer Vertex70 (Bruker Corporation, Billerica, Massachusetts, United States) equipped with a single-bounce diamond attenuated total reflectance (ATR) accessory. Analysis was employed to evaluate the purity of the recovered synthetic fibres after enzymatic hydrolysis. A reference analysis was performed on virgin PET and pure cellulose to distinguish the characteristic peaks of cellulose and synthetic material. Each sample underwent a total of 40 scans within the wavenumber range of 4000 cm<sup>-1</sup> to 650 cm<sup>-1</sup>. Subsequently, the data were normalized within the defined range from 2600 to 2500 cm<sup>-1</sup>, as there are no characteristic peaks present in this particular area (Mihalyi et al., 2023).

### 3. Results and discussion

#### 3.1. Pretreatment methods for enzymatic cellulose hydrolysis

In a first step, various pretreatment strategies to enhance enzymatic hydrolysis of cellulose were compared. Pretreatment of cotton with NaOH and trifluoroacetic acid (TFA) led to yields of enzymatic hydrolysis which were twice as high as the non-pretreated reference. Shredding (Shred) demonstrated higher values in sugar release and mass loss and was subsequently used as pre-pretreatment for further applications. Steamexplosion (Stex, 140 °C, 2 min) and electron beam irradiation (EBI, 75 kGy) did not contribute to an enhanced yield. On the contrary, they even led to lower values (Fig. 2).

#### 3.2. Statistical model for polyester and cellulose mass loss

Statistical analysis was based on mass loss as response. Pure polyester after pretreatment (design 1) and pure cellulose after pretreatment and enzymatic hydrolysis (design 3) were analyzed at three different pretreatment temperatures (Fig. 3): 10 °C (optimum temperature for later applications), 50 °C (highest temperature), and –15 °C (lowest temperature at which a model could be formed under the specified conditions).

A model could not be formed for cellulose pretreatment without subsequent enzymatic hydrolysis (design 2) due to lack of significance. A trend was observed where increasing temperatures and concentrations resulted in stronger mass reduction. The highest mass loss observed was 2.11 % (50 °C, 30 % NaOH and 12 % urea). However, at lower temperatures, the mass of the cellulose decreased after pretreatment up to 0.23 %. The relationship between pretreatment level and mass loss was not strictly linear and may have been influenced by minor losses during the washing step.

Analysis of variance (ANOVA) of design 1 showed that temperature<sup>2</sup> (*p*-value = 3.94 • 10<sup>-7</sup>), temperature (*p*-value = 2.09 • 10<sup>-5</sup>), NaOH-temperature interaction (*p*-value = 1.68 • 10<sup>-5</sup>), NaOH (*p*-value = 5.79 • 10<sup>-3</sup>) and NaOH-urea interaction (*p*-value = 3.51 • 10<sup>-2</sup>) had significant impacts on polyester mass loss. Urea (*p*-value = 0.14) and temperature-urea interaction (6.71 • 10<sup>-2</sup>) were not significant but were still included for modelling to enhance accuracy. A reduced quadratic model (*p*-value = 6.4 • 10<sup>-8</sup>, *p*-value lack of fit = 0.14, R<sup>2</sup> = 0.95) was built based on these factors. Eq. (4) can be utilized to assess the impact of NaOH (A), temperature (B) and urea (C) on polyester mass loss:

$$\text{polyester mass loss} = 7,38 - 0,23 A - 0,66 B - 0,63 C + 0,02 AB + 0,01 BC + 0,01 B^2. \quad (4)$$

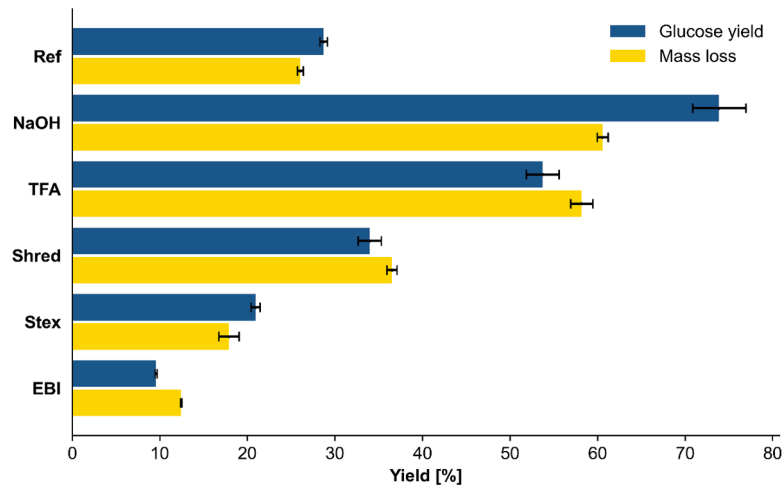


Fig. 2. Comparison of different pretreatment methods for cellulosic textiles prior to enzymatic hydrolysis in terms of glucose yield and mass loss; Ref = reference without pretreatment, NaOH = NaOH-pretreated, TFA = trifluoroacetic acid pretreatment, Shred = shredded (4 mm), Stex = Steamexplosion, EBI = Electron beam irradiation ( $n = 3$ ).

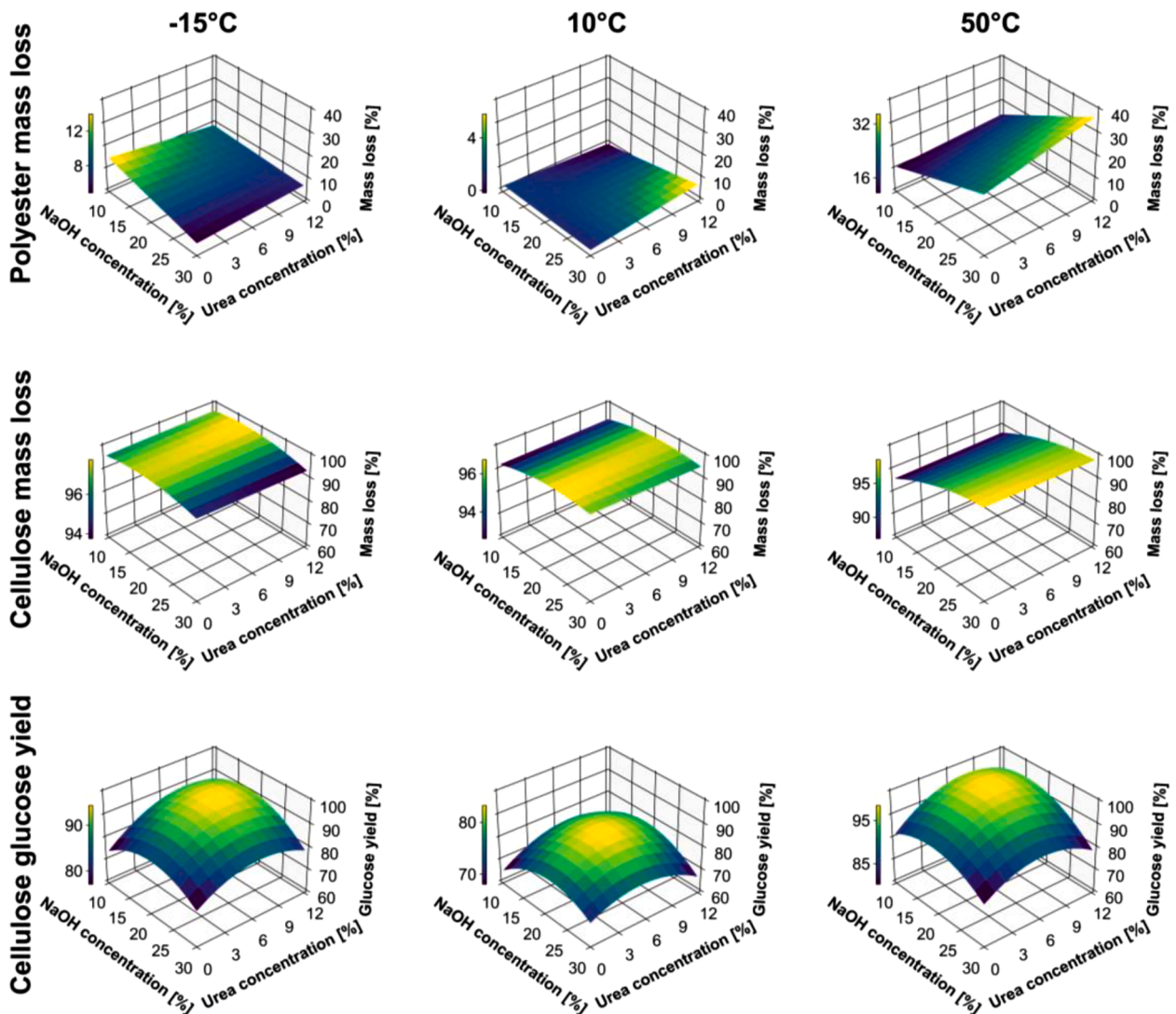


Fig. 3. Comparison of models for mass loss of pure polyester after pretreatment, and mass loss and glucose yield of pure cellulose after pretreatment followed by enzymatic hydrolysis at  $-15\text{ }^{\circ}\text{C}$ ,  $10\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$ .

The model indicates that temperatures around  $-10\text{ }^{\circ}\text{C}$  promoted the degradation of the polyester at NaOH concentrations  $<15\%$ , whereas high temperatures ( $>40\text{ }^{\circ}\text{C}$ ) favored the degradation at high NaOH concentrations ( $>25\%$ ). The effect at high NaOH concentrations was intensified with increasing urea concentration resulting in a mass reduction up to  $36.42\%$  ( $50\text{ }^{\circ}\text{C}$ ,  $30\%$  NaOH and  $12\%$  urea).

ANOVA data for mass loss of cellulose after pretreatment and enzymatic hydrolysis (design 3, response 1) demonstrated the significance of NaOH-temperature interaction ( $p$ -value =  $6.96 \cdot 10^{-11}$ ), NaOH ( $p$ -value =  $2.26 \cdot 10^{-7}$ ),  $\text{NaOH}^2$  ( $p$ -value =  $6.23 \cdot 10^{-5}$ ) and temperature ( $p$ -value =  $1.07 \cdot 10^{-5}$ ). Temperature-urea interaction ( $p$ -value =  $7.4 \cdot 10^{-2}$ ) was again included and a reduced quadratic model ( $p$ -value =  $2.05 \cdot 10^{-10}$ ,  $p$ -value lack of fit =  $0.34$ ,  $R^2 = 0.96$ ) was formed. Influences of the independent variables can be calculated using Eq. (5):

$$\text{cellulose mass loss} = 96,19 + 1,97 A - 1,41 B + 3,96 AB - 0,53 AC - 2,48 A^2. \quad (5)$$

Mass loss of pretreated and partially hydrolyzed cellulose behaved similarly to polyester mass loss, whereby the influence of urea was weaker according to the model. A maximum mass loss of  $98.72\%$  after pretreatment and 24 h hydrolysis was achieved ( $50\text{ }^{\circ}\text{C}$ ,  $30\%$  NaOH and  $0\%$  urea).

Apart from cellulose, cotton comprises at least  $2\%$  of water-insoluble extractives, waxes, proteins and pectin (Candido, 2021). This indicates that  $98.72\%$  might have been the maximum possible mass loss. The presence of extractives was confirmed by a qualitative GC-MS analysis (data not shown) of the residue obtained after hydrolysis. In design 3, both glucose yield and mass loss were investigated as response variables with the intention to check whether the mass loss corresponds to the formation glucose. A model was further developed for glucose yield after pretreatment and 24 h hydrolysis (design 3, response 2), which resulted in a distinct model compared to mass loss:  $\text{NaOH}^2$  ( $p$ -value =  $6.13 \cdot 10^{-4}$ ), NaOH-temperature interaction ( $p$ -value =  $7.62 \cdot 10^{-4}$ ) and temperature ( $p$ -value =  $8.55 \cdot 10^{-3}$ ) were significant while NaOH ( $p$ -value =  $3.90 \cdot 10^{-2}$ ), NaOH-urea interaction ( $p$ -value =  $0.38$ ), temperature<sup>2</sup> ( $p$ -value =  $0.32$ ), urea<sup>2</sup> ( $p$ -value =  $0.53$ ) and temperature-urea interaction ( $p$ -value =  $0.74$ ) were not significant but still included to develop a reduced quadratic model ( $p$ -value =  $7.35 \cdot 10^{-5}$ ,  $p$ -value lack of fit =  $0.94$ ,  $R^2 = 0.88$ ) summarized in Eq. (6):

$$\text{cellulose glucose yield} = 88,32 + 5,24 A - 7,58 B + 11,39 AB + 2,48 AC - 0,92 BC - 19,04 A^2 - 6,19 B^2 - 2,56 C^2. \quad (6)$$

The disparity between the responses may arise from the effect indicated by design 2. Due to the lack of significant correlation between pretreatment conditions and mass loss of cellulose after pretreatment, the actual effect or impact of the pretreatment on glucose yield cannot be determined as glucose yield after pretreatment and hydrolysis is related to the mass of cellulose prior to pretreatment. This tendency is supported by further analysis. For subsequent experiments, only mass loss was used as the response variable. In order to provide a complete comparison of cellulose and polyester mass loss, the 3D models for glucose yield of cellulose pretreatment and hydrolysis (design 3, response 1) were added to Fig. 3.

### 3.3. Effects of pretreatment on polyester and cellulose

The effect of the pretreatments on pure cellulose was investigated by determination of molecular weight (Mw) of fibres and analysis of the remaining NaOH/urea solutions for released glucose and hydroxycarboxylic acids. Statistically significant changes ( $p$ -value  $<0.05$ ) in cellulose Mw were found for NaOH  $>20\%$  independent from urea concentration. Temperatures of  $-20\text{ }^{\circ}\text{C}$  resulted in higher molecular weight (Mw), suggesting the occurrence of cross-linking reactions as also observed previously (Fauziyah et al., 2019; Cai et al., 2004; Qi et al., 2008; Weng et al., 2004). However, Mw of cellulose fibres decreased as the temperature and solvent concentration increased, ranging from  $1281.9 \pm 3.1\text{ kg mol}^{-1}$  for the untreated cellulose fibres to  $1146.4 \pm 14.8\text{ kg mol}^{-1}$  for pretreatment at highest level ( $50\text{ }^{\circ}\text{C}$ ,  $30\%$  NaOH and  $12\%$  urea). These findings are in agreement with previous studies

(Wang et al., 2008; Qi et al., 2008). In accordance with the drop in Mw of cellulose, short chain hydroxycarboxylic acids were identified within spent NaOH/urea-solution at  $50\text{ }^{\circ}\text{C}$ ,  $30\%$  NaOH and  $0\%$  urea: lactic acid ( $13.57 \pm 0.05\text{ mg g}^{-1}$ ), glycolic acid ( $14.39 \pm 0.16\text{ mg g}^{-1}$ ), hydroxyisobutyric acid ( $2.13 \pm 0.05\text{ mg g}^{-1}$ ) and 3-hydroxypropanoic acid ( $5.94 \pm 0.08\text{ mg g}^{-1}$ ). Those carboxylic acids are known products of alkaline thermochemical degradation of cellulose (Niemelä, 1990). Nonetheless, released glucose was not detected in any of the NaOH/urea solutions. These analyses support the trend that cellulose undergoes slight degradation during pretreatment at higher level, resulting in the formation of short chain hydroxycarboxylic acids rather than glucose.

In order to identify the impact of the pretreatment on polyester, intrinsic viscosity (IV) and crystallinity index ( $X_c$ ) were determined on polyester fibres after pretreatment. Analogous to the Mw for cellulose, the IV for polyester also decreased more strongly with increasing pretreatment level (Fig. 4). IV ranges from  $0.629 \pm 0.011$  for untreated polyester to  $0.565 \pm 0.007$  at  $50\text{ }^{\circ}\text{C}$ ,  $30\%$  NaOH and  $12\%$  urea. Nevertheless, the decrease exhibited statistical significance solely at  $50\text{ }^{\circ}\text{C}$  and  $>20\%$  NaOH. IV values for polyester after NaOH/urea treatment at moderate temperatures are comparable to others (Gholamzad et al., 2014). Due to an additional peak in XRD scattering curves, probably caused by impurities or residues of NaOH/urea, determination of crystallinity index was not valid for all conditions, especially at higher

levels. The crystallinity index of polyester was  $0.33 \pm 0.04$  for the evaluated samples, and no significant deviation was observed, which suggests that crystallinity remained relatively constant. Despite the decrease in molecular weight indicated by IV measurements, the crystallinity of polyester appeared to remain unchanged, highlighting the non-uniform representation of crystalline and amorphous regions within the samples.

### 3.4. Calculated model for polyester and cellulose and verification

The calculated model yielded identical ANOVA data and an identical equation to design 1 for polyester mass loss as the first response variable. For the second response variable, cellulose mass loss, the ANOVA data

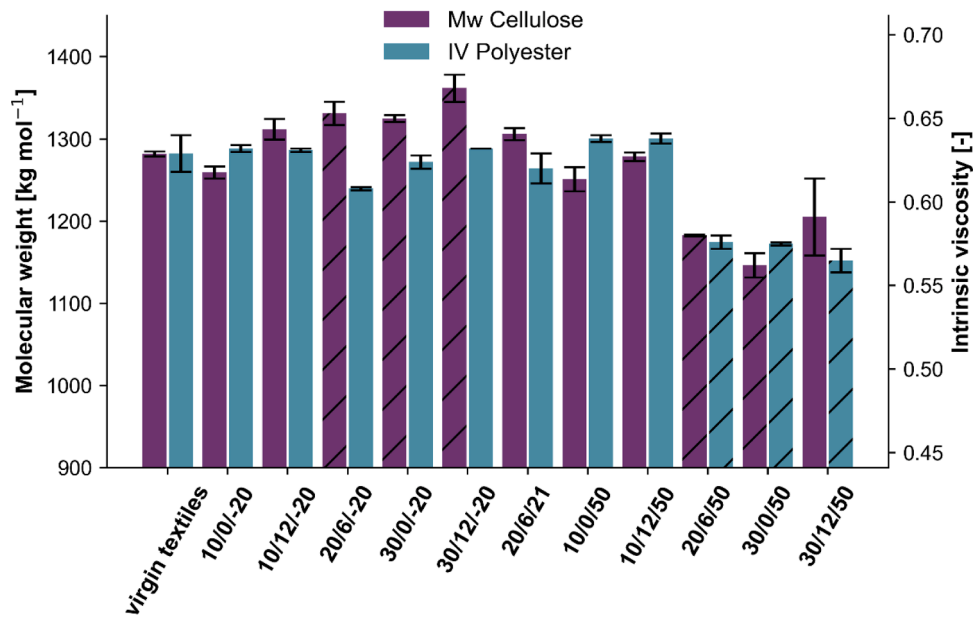


Fig. 4. Mw of cellulose and IV polyester, pretreated at diverse conditions (% NaOH/% urea/ °C Temperature), significant differences ( $p < 0.05$ ) to virgin textiles are marked /.

Table 3

Comparison of predicted values for mass loss after pretreatment of polyester and cellulose according to the calculated model and actual results of verification experiments ( $n = 2$ ).

Conditions			Mass loss polyester [%]		Mass loss cellulose [%]	
NaOH [%]	Temperature [°C]	Urea [%]	predicted	actual	predicted	actual
29.6	4.0	0.0	0.38	1.16 ± 0.22	95.62	95.89 ± 0.31
19.0	34.0	2.2	8.11	6.21 ± 0.16	94.75	95.67 ± 0.17
10.9	43.0	6.2	8.63	8.84 ± 0.12	88.27	87.18 ± 0.61
5.7	46.0	2.1	6.39	6.99 ± 0.16	81.33	34.45 ± 0.03

was slightly modified: NaOH-temperature interaction ( $p$ -value =  $1.54 \cdot 10^{-7}$ ), NaOH ( $p$ -value =  $1.65 \cdot 10^{-5}$ ),  $\text{NaOH}^2$  ( $p$ -value =  $5.42 \cdot 10^{-4}$ ) and temperature ( $p$ -value =  $3.77 \cdot 10^{-3}$ ), temperature-urea interaction ( $p$ -value = 0.30), reduced quadratic model ( $p$ -value =  $2.06 \cdot 10^{-8}$ ,  $p$ -value lack of fit = 0.99,  $R^2 = 0.92$ ). The modified interactions of the variables are given in Eq. (7):

$$\text{cellulose mass loss} = 95,99 + 2,10 A - 1,34 B + 3,88 AB - 0,45 AC - 2,32 A^2. \tag{7}$$

To establish a proof of concept, a pretreatment leading to low polyester degradation and high cellulose degradation and a pretreatment leading to higher polyester degradation and medium cellulose degradation were chosen to be experimentally verified. Additionally, randomly selected conditions within the range of the model and one outside of the specified range of the model with desirabilities  $>0.85$  were verified with the same methodology as for design 1 and design 3 (Table 3). Within the tested range, deviations of  $<2\%$  were observed, indicating a high level of accuracy for both polyester and cellulose under

Table 4

Optimization of pretreatment conditions for enzymatic hydrolysis of cotton in textile blends with polyester ( $n = 2$ ).

Group	NaOH [%]	Temperature [°C]	Urea [%]	Mass loss [%]	Glucose yield [%]	Polyester content [%]
1	26.6	7.0	0	28.46 ± 0.66	62.50 ± 3.75	86.40 ± 1.96
2	21.9	11.4	0	33.17 ± 1.04	79.71 ± 3.96	91.26 ± 0.91
3	20.7	13.4	0	31.30 ± 1.17	77.64 ± 1.51	88.98 ± 0.13
4	13.9	7.0	12	31.39 ± 0.68	85.13 ± 1.97	95.86 ± 0.87

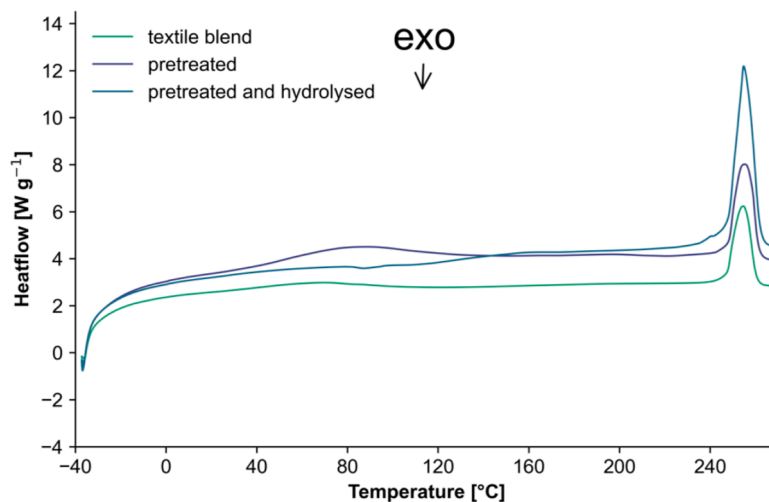
these conditions. However, when conditions exceeded the tested range, the model accurately predicted true values for polyester mass loss, but significant deviations were observed between the predicted values and the actual values for cellulose.

### 3.5. Optimisation with blended textiles

The conditions meeting the criteria of minimum polyester mass loss and maximum cellulose mass loss were identified through the use of a

numerical optimization tool within the designated range. Analysis of the data revealed that these conditions, which appeared to fulfil the desired conditions, are found at temperatures ranging from 6.2 °C to 13.3 °C. As some conditions showed close similarities and due to inherent technical limitations, that make it difficult to differentiate precisely in the settings, conditions were categorized into four groups. The conditions within these four groups were applied to blended textiles for verification analogue to hydrolysis applied in design 3 (Table 4).

With the aim to determine the optimal group of conditions, the evaluation considered - unlike previous experiments - multiple factors



**Fig. 5.** DSC analysis for determination of characteristic melting peak for polyester (exo down) with untreated textile blend, pretreated textile blend and pretreated and enzymatically hydrolyzed textile blend.

**Table 5**

Mass loss, polyester and glucose content of the solid fraction of polyester / cotton textile blends before and after pretreatment and enzymatic hydrolysis. ( $n = 3$ ).

	Mass loss [%]	Polyester content [%]	Glucose content [%]
textile blend	–	$67.67 \pm 0.67$	$34.06 \pm 1.01$
pretreated	<0.5	$68.39 \pm 0.71$	$28.72 \pm 0.64$
pretreated and hydrolyzed	$37.74 \pm 0.51$	$97.30 \pm 2.34$	$0.16 \pm 0.07$

and not only mass loss alone. The objective was to achieve a high polyester content to ensure maximum cellulose degradation and abundant glucose yield as the hydrolysate is ideally intended for utilization in fermentation processes. Based on these evaluation criteria, it turned out that group 4 (13.9 % NaOH, 7 °C, 12 % urea) exhibited the best performance. Group 4 was, therefore, chosen for further experiments aiming for complete cellulose hydrolysis.

The glucose content of the fibres slightly decreased after pretreatment and markedly after hydrolysis, while polyester content, visible due

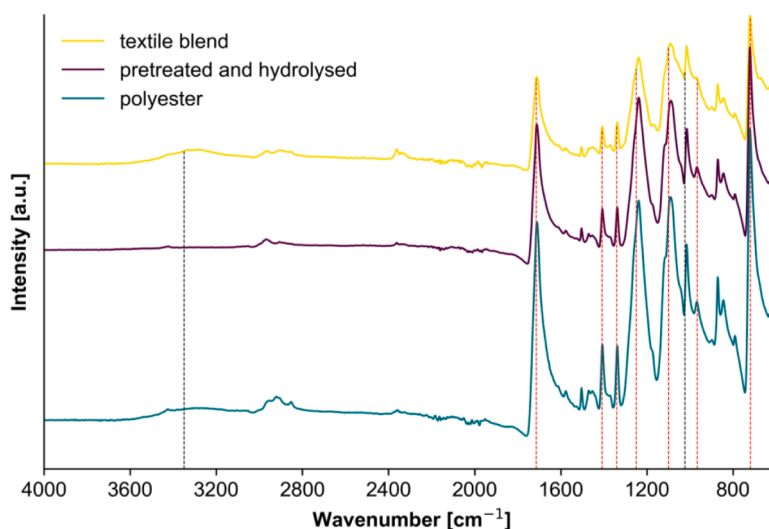
to the characteristic melting peak in DSC (Fig. 5), increased marginally after pretreatment and approaches 100 % after pretreatment and hydrolysis (Table 5). These observations provide additional evidence supporting the occurrence of cellulose degradation during the pretreatment process.

Additionally, FTIR analysis was performed to prove purity of regenerated polyester fibres. Compared to the untreated textile blend and to pure polyester, it turned out that peaks characteristic for cellulose ( $3350 \text{ cm}^{-1}$  O-H stretch, alcohol;  $1020 \text{ cm}^{-1}$  C-O stretch, aliphatic ether) decreased, while peaks characteristic for PET ( $1715 \text{ cm}^{-1}$  C=O stretch, Ester;  $1410 \text{ cm}^{-1}$  C-H plane bending, C-C stretching;  $1341 \text{ cm}^{-1}$  C-H wagging;  $1250 \text{ cm}^{-1}$  C-O-C stretch, Ester;  $1120 \text{ cm}^{-1}$  C-O stretch, Ester;  $970 \text{ cm}^{-1}$  O-CH<sub>2</sub> stretch, C=O stretch;  $720 \text{ cm}^{-1}$  C-H bending, aromatic ring) increased (Fig. 6) (Donelli et al., 2009; Gritsch et al., 2023).

The applied methodology ultimately resulted in the successful realization of the objective, namely achieving complete cellulose decomposition while preserving the integrity of polyester.

#### 4. Conclusion and outlook

The past two decades have witnessed a substantial global rise in



**Fig. 6.** FTIR analysis of untreated textile blend, textile blend pretreated and enzymatically hydrolyzed, and virgin polyester. Normalized between 2600 and 2500  $\text{cm}^{-1}$ . Characteristic peaks for cellulose are marked in black, whereas characteristic peaks for polyester are marked in red.



textile production and consumption, resulting in significant environmental and societal risks due to the absence of effective waste management strategies. In this study, enzymatic hydrolysis of cotton components in textile blends with polyester was investigated with a particular emphasis on the optimization of NaOH/urea pretreatment by applying design of experiment studies. The implementation of reduced quadratic models enabled the description of complex interplay between NaOH concentration, temperature and urea concentration. Mass loss analysis revealed that NaOH/urea pretreatment led to degradation of polyester, along with a minor degradation of cellulose occurring already during the pretreatment process. However, there is a sensitive balance point since the extent of degradation depends on the specific conditions employed.

Additional analyses focused on assessing the molecular changes and properties of cellulose and polyester fibres under the influence of NaOH/urea pretreatment.

One notable finding was the trend observed in the Mw of cellulose. At low temperatures, Mw was higher compared to untreated reference, indicating the presence of cross-linking reactions. However, higher temperatures and NaOH concentrations resulted in a decrease in Mw.

Assessing spent NaOH/urea-solution at high temperature and high concentrations revealed that cellulose undergoes slight degradation, resulting not in glucose but in the formation of hydroxycarboxylic acids.

In contrast, analysis of polyester fibres showed a decrease in intrinsic viscosity (IV) with intensified pretreatment conditions. This decrease in IV indicated a reduction in molecular weight of the polyester chains, likely due to hydrolysis or cleavage of the ester bonds. However, no significant decrease in crystallinity was observed, suggesting that the pretreatment conditions had a limited impact on the overall crystalline structure of polyester.

It was found that by adjusting the pretreatment conditions in terms of NaOH concentration, urea concentration and temperature, it was possible to achieve desired results in terms of minimal polyester degradation during pretreatment and maximal cellulose degradation after pretreatment and subsequent enzymatic hydrolysis. The key parameters that influence these results are temperature range of 6.2 °C to 13.3 °C and the choice of NaOH concentrations. Specifically, using NaOH concentrations ranging from 20.7 % to 26.6 % with 0 % urea or a combination of 13.9 % NaOH and 12 % urea proved to be effective and demonstrated an almost complete elimination of cellulose within a blended textile (35 % polyester, 65 % cotton), indicating the successful achievement of the desired objective.

These outcomes have significant implications for sustainable textile recycling and circularity: The preserved polyester can be effectively transformed into new fibres and, consequently, into textiles, maintaining the same quality standards as virgin polymer. Moreover, the glucose derived from hydrolysis can be employed in fermentation processes producing e.g. biopolyesters, promoting the realization of textile biorefinery concepts.

#### Declaration of generative AI in scientific writing

During the preparation of this work Katharina Steiner used ChatGPT in order to improve readability and language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

#### CRediT authorship contribution statement

**Katharina Steiner:** Investigation, Formal analysis, Visualization, Methodology, Writing – original draft. **Viktoria Leitner:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Franz Zepetzauer:** Investigation, Formal analysis, Supervision. **Doris Ostner:** Investigation, Formal analysis, Project administration. **Christoph Burgstaller:** Writing – review & editing, Funding acquisition. **Harald Rennhofer:** Investigation, Formal analysis, Supervision. **Andreas Bartl:**

Methodology, Supervision, Writing – review & editing. **Doris Ribitsch:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Georg M. Guebitz:** Supervision, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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