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Reclaiming the Value of Cotton Waste Textiles: A New Improved Method to Recycle Cotton Waste Textiles via Acid Hydrolysis

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Abstract: The fashion industry is becoming one of the largest emitters worldwide due to its high consumption of raw materials, its effluents, and the fact that every garment will eventually contribute to the vast amount of waste being incinerated or accumulating in landfills. Although fiber-to-fiber recycling processes are being developed, the mechanical properties of the textile fibers are typically degraded with each such recycle. Thus, tertiary recycling alternatives where textiles are depolymerized to convert them into valuable products are needed to provide end-of-life alternatives and to achieve circularity in the fashion industry. We have developed a method whereby cotton waste textiles are depolymerized to form a glucose solution, using sulfuric acid as the sole catalyst, with a high yield (>70%). The glucose solution produced in this process has a high concentration (>100 g/L), which reduces the purification cost and makes the process industrially relevant. This method can be applied regardless of the quality of the fibers and could therefore process other cellulosic fibers such as viscose. The glucose produced could subsequently be fermented into butanediol or caprolactam, precursors for the production of synthetic textile fibers, thus retaining the value of the waste textiles within the textile value chain.

Keywords: waste textiles; cotton; recycling; valorization; acid hydrolysis; sulfuric acid

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1. Introduction

The environmental impact of the textile industry is immense, not only because of its high consumption of raw materials and its effluents, but also because every piece of textile produced will sooner or later contribute to the vast amount of waste textiles [1,2]. The fashion industry struggles with misinformation and, consequently, there is uncertainty regarding the exact amount of waste textiles being generated today [3]; however, according to Ruiz, total textile fiber production is expected to surpass 120 million tons annually by 2025 [4]. Due to wear and tear, these textiles will eventually be damaged beyond usefulness and, as such, all textiles are ultimately discarded. Only a small fraction of these waste textiles is currently being recycled, the vast majority either being landfilled or incinerated [5]. The reason for this lies in the complexity of the material [2]. Firstly, textiles consist of a combination of components, such as buttons, seams, and zippers, which must be separated from the actual fabric. Secondly, fabrics often consist of a mixture of several types of fiber that may differ considerably from each other on the polymer level. These fibers thus have very different chemical and mechanical properties, and there is no single method of recycling all types of fiber. Before any form of recycling can take place, the textiles must therefore be sorted based on the types of fiber they include. Polyester and cotton are by far the most frequently used kinds of fibers, and, in total, more than 95% of all fibers produced today are either synthetic or cellulose-based [6].

Since cellulose-based fibers constitute more than a third of all textile fibers produced annually, methods for recycling cellulosic textiles are a suitable target for research. Various recycling methods have been developed to recycle cotton textiles, which is by far the most common cellulose-based fiber [6]. One example is that of the Swedish company Renewcell, which turns cotton waste textiles into dissolving pulp [7]; however, existing methods have limitations. There is currently no commercial-scale process for cellulosic textile recycling other than on the fiber and polymer level, which means that the polymers, or entire fibers, are extracted in some way, treated, and turned into new fibers that can be used to produce new textiles. Such processes require a certain quality of polymers and fibers; if they are too short or damaged, they cannot be recycled in this manner. Thus, since the degree of polymerization of cellulosic fibers decreases during use and with each regeneration process [8,9], there is need for additional, tertiary recycling methods capable of recycling, or in other ways valorizing, textile fibers, regardless of their quality.

One promising alternative for valorization of waste textiles of low quality is to degrade the polymers to their monomeric constituents. These monomers can then be converted into monomers for the production of synthetic textiles, valuable chemicals, or biofuel. In the case of cellulose, as in cellulose-based waste textiles such as cotton, hydrolysis using sulfuric acid is an interesting option. Acid hydrolysis of cellulose, and lignocellulosic biomass in general, has been studied since 1819 and has, during the last two centuries, seen a lot of development, improvement, and implementation [10–18]. The two-step sulfuric acid hydrolysis is a particularly effective variant, whereby the substrate is exposed to hydrolysis at different conditions with regard to temperature and concentration of sulfuric acid. Indeed, two-step hydrolysis using sulfuric acid is a common method to determine the content of structural carbohydrates in lignocellulosic samples [19,20]. Cotton waste textiles, being a source of relatively pure cellulose, share similarities with general lignocellulosic biomass in that it is remarkably hard to hydrolyze into reducing sugars [21,22]. While virgin cotton has a relatively high resistance toward hydrolysis, due to its high degree of crystallinity and long polymeric chains [11–14,23], cotton once converted into textiles has been shown to exhibit even higher resistance towards hydrolysis. Virgin cotton has been reported to hydrolyze completely at room temperature in 55% sulfuric acid, while similar and more drastic conditions failed to achieve the same when cotton textiles were used as the substrate [22,24]. These similarities between cotton waste textiles and lignocellulosic biomass have led to several successful studies on the use of techniques typical for hydrolysis of general biomass for saccharifying cotton waste textiles [21,25].

We have recently developed a method whereby cotton waste textiles can be depolymerized to form a glucose solution [22]. We succeeded in transforming the cotton textiles into an acidic glucose solution, using sulfuric acid as the sole catalyst, while achieving a high yield. While other researchers have managed to hydrolyze cotton textiles before, no one has, to the best of our knowledge, been able to produce a highly concentrated product, while at the same time maintaining a high yield. The purpose of this study was thus to optimize the operating parameters of this newly developed process as a step toward industrial commercialization, by producing a highly concentrated product while maintaining a high yield. Using sulfuric acid as the sole catalyst improves the production rate considerably compared to an enzymatic approach and a concentrated product allows for easier separation and downstream handling. In summary, the operating parameters of this newly developed process were optimized in this study by testing and evaluating the effect of different combinations of temperature and acid concentrations. It was concluded that it is possible to use the proposed technique to produce glucose at a high concentration (>100 g/L) and at a high yield (>70%). The reactivity and recyclability of the residual waste formed during treatment were also investigated.

2. Materials and Methods

2.1. Collection and Preparation of Cotton Waste Textiles

The cotton waste textiles used in this study were discarded bed linens unfit for reselling, and labelled 100% cotton, donated by the authors' friends and family, employees at the Department of Chemical Engineering at Lund University, and a collection point of a Swedish organization that collects and sorts textiles for charity and recycling. The cotton waste textiles were used as a proxy for cellulose-based textiles in general. It is by far the most common cellulose-based textile, and if the process works for a material with such a high resistance towards hydrolysis as cotton waste textiles, it should be no problem adapting it to other cellulosic fibers, such as viscose waste textiles [6,14,18,22,26]. Prior to the experiments, buttons, seams, labels, and other parts not made of cotton were removed from the textiles. The textiles were subsequently cut into smaller pieces, approximately 2 by 2 cm, using a circular textile knife (Ø 45 mm, Stoff & Stil, Malmö, Sweden). The material was then mixed thoroughly to ensure representability of the samples.

2.2. Two-Step Acid Hydrolysis

Several two-step acid hydrolysis experiments were conducted, consisting of pre-hydrolysis with concentrated sulfuric acid, followed by post-hydrolysis with dilute sulfuric acid (Figure 1).

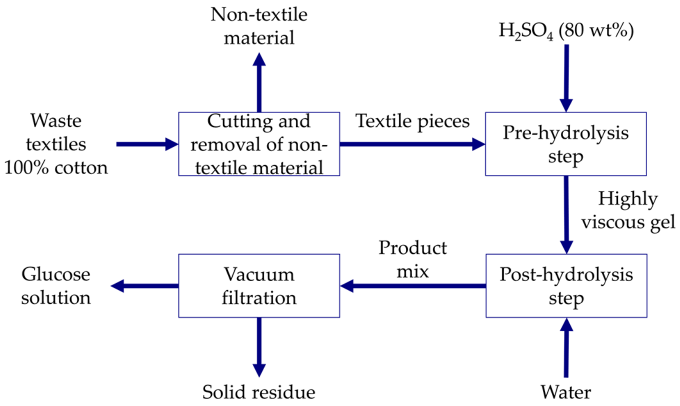

Figure 1. Schematic of the two-step textile hydrolysis process using different concentrations of sulfuric acid.

2.2.1. Pre-Hydrolysis

The pre-hydrolysis step was performed by exposing 100 g of dry waste textiles to 134 g of an 80 wt.% sulfuric acid solution, corresponding to a solids loading of 0.744 g dry textiles/g sulfuric acid solution. Treatment was conducted in a water bath at a temperature of 30 °C for one hour, according to the method described in our previous study [22].

The influence of the concentration of sulfuric acid in the pre-hydrolysis step on the crystallinity of the cellulose from the cotton waste textiles was investigated. The samples were prepared by exposing 5 g of dry waste textiles to 6.72 g of sulfuric acid of different concentrations (60 wt.%, 72 wt.%, and 80 wt.%) at 30 °C for 1 h. These samples, together with a sample of untreated cotton waste textiles, were then studied using wide-angle X-ray scattering (WAXS) analysis with an Anton Paar SAXSpoint 2.0 system (Anton Paar, Graz, Austria) equipped with a Microsource X-ray source (Cu K-alpha radiation, wavelength 0.15418 nm) and a Dectris 2D CMOS Eiger R 1M detector (DECTRIS, Baden-Daettwil, Switzerland) with a 75 × 75 μm^2 pixel size. All measurements were performed with a beam of approximately 500 µm in diameter and a beam path pressure of about 1–2 mbar. The sample-to-detector distance was 109.1 mm during the measurements. Samples were mounted on a Multi-Paste holder (Anton Paar, Graz, Austria). Six frames of 15-min duration were read from the detector, giving a total measurement time of 1.5 h per sample. The transmittance was determined and used to scale the intensity. The software used for instrument control was SAXSdrive, version 2.01.224, and post-acquisition data processing was performed using SAXSanalysis, version 4.01.047 (both from Anton Paar, Graz, Austria).

2.2.2. Post-Hydrolysis

The post-hydrolysis step was performed by diluting the gel formed in the pre-hydrolysis step with varying amounts of water, in order to achieve concentrations of sulfuric acid in the mixture between 10 wt.% and 30 wt.%. The samples were thoroughly mixed and treated in an autoclave for one hour at 80 °C, 100 °C, or 121 °C. After autoclaving, the samples were cooled to 80 °C, before being evacuated from the autoclave and vacuum filtered through a filter cloth with a pore size of 100 µm. The liquid and solid fractions were subjected to further analysis.

2.3. Recyclability of the Solid Residue

The recyclability of the solid residue from the process was investigated by treating an amount corresponding to 7 g dry matter of solid material recovered as solid residue from the post-hydrolysis step of a previous cycle of treatment, using two different approaches. In the first approach, called the dry method, the solid residue recovered after vacuum filtration was dried and milled using a knife mill (Retsch GmbH, Haan, Germany) and sieved to obtain fractions with a size of 1 mm. The dried and milled solid residue was then mixed with new cotton waste textiles and subjected to a second cycle of treatment. In the second cycle, the pre-hydrolysis step was performed as described in Section 2.2.1, and the post-hydrolysis step was carried out at 100 °C with 15 wt.% sulfuric acid for one hour.

In the second approach, called the wet method, the solid residue was dispersed in water and then added to the post-hydrolysis step in the second cycle of treatment. The conditions in the post-hydrolysis step were the same as in the dry method, namely 100 °C and 15 wt.% sulfuric acid. In both recycling approaches, the total mass used was halved compared to the experiments described in Section 2.2, and the mass ratio of substrate (cotton waste textiles and recycled solid residue) to sulfuric acid was kept at the same level in the post-hydrolysis step.

2.4. Compositional Analysis of Cotton Waste Textiles and the Products following Two-Step Acid Hydrolysis

The total solids (TS) content of the cotton waste textiles was analyzed in triplicate by drying the textiles in an oven (105 °C) overnight and weighing. The cellulose content was analyzed according to NREL standards [19], with the exception that, instead of being milled through a 1 mm screen, the textiles were cut into lengths of 10 mm, according to ISO 1833-1 for quantitative chemical analysis of textiles [27]. The fraction assigned to acid-insoluble lignin using the protocol developed by Sluiter et al. was denoted non-cellulosic material, since the residual material after completed hydrolysis was an unidentified mixture of non-cellulosic threads, dyes, and other additives typically used in textile manufacture, and impurities introduced during the lifetime of the textiles. Cellulose analysis was performed in sextuplicate.

Glucose and degradation by-products from the compositional analysis and the acid hydrolysis experiments on cotton waste textiles were analyzed by high-performance liquid chromatography (HPLC) using a Shimadzu LC-20 AD HPLC system equipped with a Shimadzu RID 10A refractive index detector (Shimadzu Corporation, Kyoto, Japan). The chromatography column used together with the HPLC system was an Aminex HPX-87H, with a Cation-H MicroGuard column (Bio-Rad Laboratories, Hercules, CA, USA) at 50 °C. The eluent was 5 mM sulfuric acid, at a flow rate of 0.5 mL/min and a pressure of 50 bar.

The TS content of the solid samples generated during acid hydrolysis was analyzed by drying the samples in an oven (105 °C) for 48 h and weighing. The water-insoluble solids (WIS) content was determined by thoroughly washing the samples before drying them in an oven (105 °C) and weighing, according to the NREL protocol developed by Sluiter et al. [28].

The TS measurements were performed in triplicate and the WIS measurements were performed in duplicate.

2.5. Collection, Two-Step Hydrolysis, and Compositional Analysis of Viscose Waste Textiles and Its Derivatives

The viscose waste textiles used in this study were sorted at, and provided by, a textile sorting facility. Only textiles consisting of 100% viscose were selected for this study. Buttons, seams, and other non-textile components were removed from the waste textiles prior to shredding into a size of approximately 3 by 3 cm and delivery.

The two-step acid hydrolysis of the viscose waste textiles was performed by first exposing 25 g of dry textiles to 126 g of 80 wt.% sulfuric acid for 1 h at 30 °C. After completed pre-hydrolysis, 568.5 g of water was added to the mixture to reach a sulfuric acid concentration of 15 wt.%. The mixture was thoroughly mixed and treated for 1 h at 121 °C in an autoclave. Upon completed post-hydrolysis, the mixture was allowed to cool before samples were taken from the supernatant.

The total solids content of the viscose waste textiles was determined gravimetrically in triplicates, before and after freeze-drying samples of around 500 mg at 25 °C. The polysaccharide content of the viscose waste textiles was analyzed following the acid hydrolysis method developed by Saeman et al. [29]. The hydrolysates from the compositional analysis of the raw material, as well as the supernatant samples from the hydrolysis experiments, were separated and quantified by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) on an ICS6000 system (Dionex, Sunnyvale, CA, USA), as described elsewhere [30]. The monosaccharide contents were calculated in reference to a standard mixture (0.005–0.01 mg/mL) containing fucose, rhamnose, arabinose, xylose, galactose, glucose, mannose, galacturonic acid, and glucuronic acid (Sigma Aldrich, Stockholm, Sweden).

2.6. Calculations

The glucose yield was calculated based on the total amount of glucose in the raw material, as determined in the compositional analysis. The total amount of glucose in the waste textiles corresponds to 1.11 times the cellulose content, since water is added to the cellulose during hydrolysis. The total amount of glucose in the solid residue used in recycling experiments was calculated twice, following two different assumptions. The first value was calculated assuming that the dry matter of the solid residue consisted only of glucan, while the second value was calculated assuming that all non-cellulosic material in the raw material was recovered in the solid residue. In both cases, the liquid trapped in the solid residue was assumed to have the same composition as the liquid product obtained from vacuum filtration where the solid residue was recovered. The glucose yield in the experiments was subsequently calculated by multiplying the glucose concentration in the liquid product by the volume of the liquid product and then dividing by the total amount of glucose in the raw material (see Equations (1)–(3)).

$$Y_{waste\ textiles} = \frac{c_{glucose}V}{\eta_{WT} m_{WT} w_{cell} \cdot 1.11} \tag{1}$$

$$Y_{mix,\ pure\ SR} = \frac{c_{glucose}V}{\eta_{WT} m_{WT} w_{cell} \cdot 1.11 + m_{SR,dry} \cdot 1.11 + \frac{m_{SR,liq}}{\rho_I} c_{glucose,I}} \tag{2}$$

$$Y_{mix,\ impure\ SR} = \frac{c_{glucose}V}{\eta_{WT} m_{WT} w_{cell} \cdot 1.11 + \left(m_{SR,dry} - m_{SR,\ non-cell}\right) \cdot 1.11 + \frac{m_{SR,liq}}{\rho_I} c_{glucose,I}} \tag{3}$$

where $Y_{waste\ textiles}$ denotes the glucose yield from waste textiles, $Y_{mix,\ pure\ SR}$ the glucose yield from a mixture of waste textiles and recycled solid residue where the solid residue is assumed to consist purely of glucan, and $Y_{mix,\ impure\ SR}$ denotes the glucose yield from a mixture of waste textiles and recycled solid residue where the solid residue is assumed to contain impurities in the form of non-cellulosic material found in waste textiles. $c_{glucose}$ denotes the glucose concentration in the liquid product, V is the volume of the liquid product, η_{WT} is the dry matter content of the waste textiles, m_{WT} is the mass of waste textiles used in the experiment, w_{cell} is the mass fraction of cellulose within the waste textiles (determined in the compositional analysis), and 1.11 is a correction factor corresponding to the weight increase when water is added to cellulose/glucan during hydrolysis. $m_{SR,dry}$ denotes the dry weight of the recycled solid residue, $m_{SR,liq}$ is the weight of the liquid trapped in the recycled solid residue (before drying), ρ_I is the density of the liquid trapped in the recycled solid residue (before drying), $c_{glucose,I}$ is the glucose concentration in the liquid trapped in the recycled solid residue (before drying), and $m_{SR,\ non-cell}$ is the dry weight of non-cellulosic material present in the recycled solid residue, assuming that all the non-cellulosic material present in the waste textiles is recovered in the solid residue after the vacuum filtration step.

Since a significant amount of material was lost during vacuum filtration after the post-hydrolysis step, i.e., neither recovered in the liquid fraction nor the solid, (see Section 3.2.2. for further discussion on material losses), the values of the glucose concentration of the liquid product obtained from the HPLC analysis required adjustment to reflect the actual glucose concentration in the liquid fraction after the post-hydrolysis step. The prolonged exposure to vacuum allowed volatile components of the mixture to evaporate and, since the most volatile component in the product mixture was water, it was assumed that these mass losses corresponded to pure water losses. Moreover, the filtration time varied depending on the conditions used in the post-hydrolysis step, which led to differences in the magnitude of the mass losses. Thus, in order to ensure valid comparisons of the glucose concentration in the different experiments, the effect of vacuum filtration was eliminated by adjusting the glucose concentrations obtained from the HPLC analysis, by assuming the mass losses during vacuum filtration to be pure water, according to Equation (4):

$$c_{glucose,adjusted} = \frac{c_{glucose} V}{V + m_{lost}/\rho_w} \tag{4}$$

where $c_{glucose,\ adjusted}$ is the concentration of glucose after the post-hydrolysis step, $c_{glucose}$ is the glucose concentration of the liquid product after vacuum filtration measured by HPLC analysis, V is the volume of the liquid product after vacuum filtration, m_{lost} is the mass lost during the vacuum filtration step, and ρ_w is the density of pure water at room temperature.

3. Results and Discussion

3.1. Composition of Cotton Waste Textiles

According to the compositional analysis, the cellulose content of the cotton waste textiles used in this study was 92% (standard deviation 1%). The blue jeans used in the study by Jeihanipour et al. were found to have a cellulose content of 93% (±1%) [21], while Buchert et al. reported that raw cotton fibers, before the addition of dyes, contained 3.6% non-cellulosic components, which corresponds to a cellulose content of 96.4% [31]. Thus, the results of the compositional analysis of the waste textiles were deemed to be consistent with previous findings.

3.2. Optimization of the Two-Step Acid Hydrolysis

3.2.1. Pre-Hydrolysis

The change in crystallinity of cotton waste textiles upon exposure to sulfuric acid at varying concentrations in the pre-hydrolysis step is shown in Figure 2. As the textiles were exposed to increasing concentrations of sulfuric acid, the distinct pattern typical of crystalline cellulose I [32] seen in the measurements on the raw material (Textiles, no acid) gradually faded away until individual equatorial reflections could no longer be distinguished (at 80 wt.% sulfuric acid). This loss of distinct equatorial reflections in the diffractogram indicates a loss of crystalline regions in the sample, i.e., the cellulose has been de-crystallized into an amorphous state [33]. As shown in our previous study, the performance of the two-step acid hydrolysis process is dependent on the sulfuric acid concentration in the pre-hydrolysis step; concentrations below 80 wt.% in the pre-hydrolysis step had a significant negative impact on the efficiency of the process [22]. The results of the WAXS measurements presented in Figure 2 illustrate the favorable effect of the high concentration of sulfuric acid in the pre-hydrolysis step, as the rate of acid-catalyzed hydrolysis of amorphous cellulose is known to be significantly higher than that of crystalline cellulose [14,18,34].

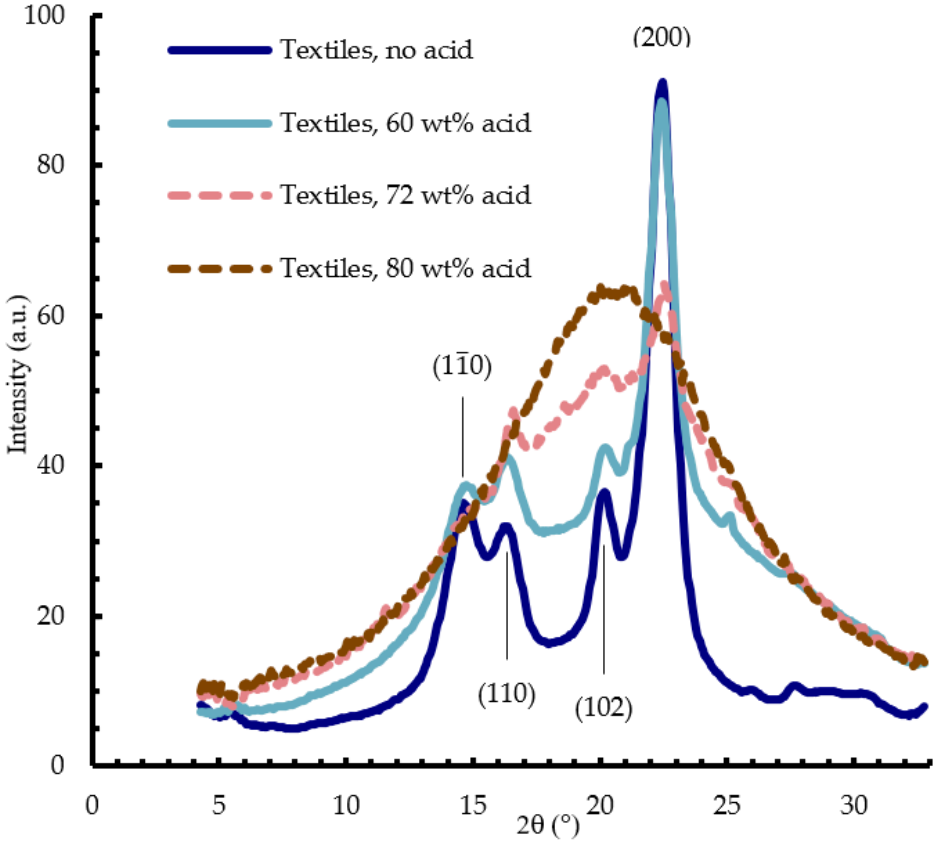

Figure 2. WAXS diffractograms measured on cotton waste textiles treated with varying concentrations of sulfuric acid in the pre-hydrolysis step.

3.2.2. Optimization of the Post-Hydrolysis Step

In general, a higher temperature and higher sulfuric acid concentration in the post-hydrolysis step led to a lower glucose yield, as can be seen in Figure 3a. The lower glucose yield at higher temperatures can be explained by increased by-product formation during experiments at 121 °C, while the presence of any by-products was below the quantification limit in experiments performed at 100 °C and 80 °C. A higher formation of by-products was expected at higher temperatures and increased acidity, as similar behavior has been reported for lignocellulosic biomass [17,35]. Increasing the concentration of sulfuric acid in the post-hydrolysis step during experiments at 121 °C did indeed increase by-product formation, which partly explains the decrease in glucose yield. However, although the glucose yield decreased in a similar manner when increasing the sulfuric acid concentration at 100 °C, the concentration of by-products remained below the quantification limit. Moreover, the increase in by-product formation did not correspond completely to a decrease in glucose production when increasing the concentration of sulfuric acid when running at 121 °C. The conversion of cellulose into hydrolysates, i.e., the fraction of cellulose that was hydrolyzed into either glucose, hydroxymethylfurfural (HMF), or levulinic acid (common by-products in the degradation of glucose and the only ones detected during the HPLC analysis), decreased with increasing concentrations of sulfuric acid, at both 100 °C and 121 °C (Figure 3b). This suggests that increasing the concentration of sulfuric acid (which corresponds to a decrease in the water content, which is consumed during hydrolysis) halts hydrolysis, leaving part of the material unreacted, possibly in the form of oligomeric sugars. To test this hypothesis, the duration of the post-hydrolysis step (100 °C and 30 wt% sulfuric acid) was increased to 3 h. When the duration was increased to 3 h, the conversion of cellulose into hydrolysates remained at 45%; however, the glucose yield decreased by eight percentage points, which corresponded to the increase in levulinic acid. The fact that the conversion of cellulose into hydrolysates remained unchanged upon increasing the temperature (from 100 °C to 121 °C) and the duration of the post-hydrolysis step (from 1 to 3 h) demonstrates that the concentration of the sulfuric acid solution had the greatest effect on the degree of hydrolysis of the raw material in the post-hydrolysis step at sufficient temperatures and residence times (100 °C, 1 h), while increasing the residence time and temperature further mainly led to increased by-product formation.

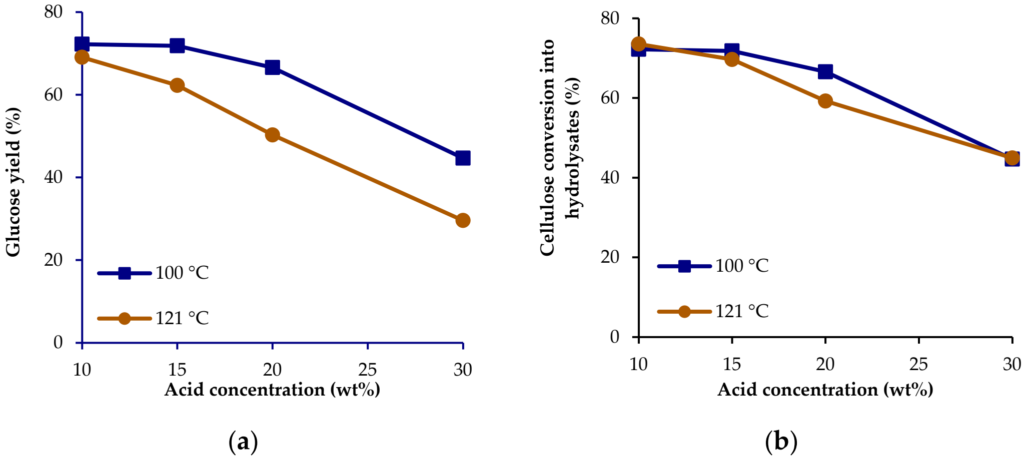

Figure 3. Glucose yield (**a**) and conversion of cellulose into hydrolysates (**b**) obtained with different combinations of sulfuric acid concentration and temperature in the post-hydrolysis step.

Interestingly, the decrease in hydrolysates with increasing concentrations of sulfuric acid did not lead to a proportional increase in solids recovery. Throughout the experiments at both 100 °C and 121 °C, the solid recovery remained about 20%. This indicates that, as the concentration of sulfuric acid was increased, a larger fraction of the cotton waste textiles was converted into oligomeric glucose chains, which were too short to be recovered in the solid residue but too long to be detected in the HPLC analysis. We found similar results in our previous study, when increasing the concentration of sulfuric acid at a high temperature (130 °C) led to an increase in the amount of material neither recovered in the solid residue nor detected as monomers in the HPLC analysis, together with higher by-product formation [22]. An alternative explanation could be the formation of unknown compounds during the treatment that might avoid detection in the HPLC analysis. Nonetheless, it has been shown that during treatment with inorganic acids, the rate of depolymerization of cellulose decreases until it levels off, after which it remains relatively unchanged despite further treatment [12]. This phenomenon has been reported more recently during the hydrolysis of cotton textiles using sulfuric acid at similar conditions to those in the present study [24], which supports the hypothesis that the material not recovered as solid residue or monomers in this study is indeed oligomeric glucose chains in the liquid product.

While the glucose yield decreased at higher sulfuric acid concentrations in the post-hydrolysis step, the glucose concentration in the liquid product increased, as can be seen in Figure 4. Although the glucose yield decreased with increasing sulfuric acid concentrations, the lower water content in the more concentrated acid led to all the components in the liquid product becoming more concentrated, including glucose.

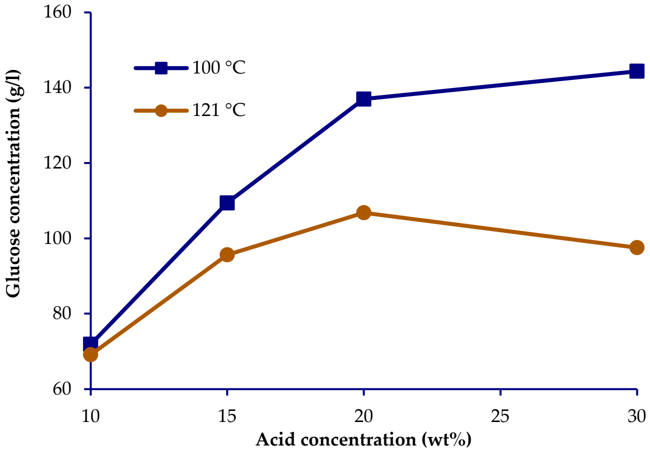

Figure 4. Glucose concentration in the liquid product at different combinations of sulfuric acid concentration and temperature in the post-hydrolysis step. The values are adjusted assuming all loss of mass during filtration was evaporated water.

As can be seen in Figure 4, the glucose concentration in the liquid product was consistently higher at a temperature of 100 °C than at 121 °C. This is consistent with the fact that more glucose is lost due to by-product formation at higher temperatures. These glucose losses became so high that when the acid concentration was increased from 20 wt.% to 30 wt.% (at 121 °C), the glucose concentration decreased, counteracting the fact that the system is 1.5 times more diluted at 20 wt.% than at 30 wt.%. This is supported by the fact that conversion of cellulose to hydrolysates was the same at both 100 °C and 121 °C with 30 wt.% sulfuric acid, indicating that by-product formation constitutes the difference between the results at the two acid concentrations. Interestingly, Figure 4 shows that the glucose concentration was consistently above 100 g/L in the experiments performed at 100 °C, except when using a sulfuric acid concentration below 15 wt.% in the post-hydrolysis step. Since by-product formation was limited at 100 °C, increasing the acid concentration in the post-hydrolysis step proved to be an effective way of increasing the glucose concentration, at the expense of the glucose yield; however, the effect was lower at sulfuric acid concentrations above 20 wt.%. Additional experiments were performed at 80 °C, but were found to be significantly inferior to 100 °C, both in terms of glucose yield and concentration due to low reactivity (data not shown).

The saccharification of lignocellulosic material using sulfuric acid in general, and two-step hydrolysis in particular, has seen detailed study before [10,15,19,34]. As can be seen in Table 1, Kong-Win Chang et al. were able to achieve almost complete hydrolysis of cellulose using concentrated sulfuric acid in the pre-hydrolysis step, followed by partial neutralization and subsequent post-hydrolysis using sodium hydroxide [17]. The yield was impressive, but the process required large quantities of sulfuric acid, resulting in a very low solids loading. However, post-consumer cotton textiles exhibit significantly higher resistance toward hydrolysis than cellulose from other sources, including virgin cotton. In an attempt to overcome the stability of cotton textiles, Sasaki et al. studied a microwave-assisted method to directly hydrolyze cotton towels [36]. The microwave-assisted direct hydrolysis had a very low glucose yield, and a subsequent enzymatic hydrolysis step was necessary to improve the process (Table 1). Similarly, Kuo et al. achieved high glucose yields by pretreating waste textiles with sulfuric acid followed by an enzymatic hydrolysis step [37]. Despite the high glucose yields achieved by Sasaki et al. and Kuo et al., both methods required the use of enzymes, and the solids loadings were notably low, which in turn led to a low glucose concentration in the solution (Table 1). At low solids loadings, the technology developed in this study was in our previous study shown to be capable of achieving glucose yields above 90% [22]. After the optimization in the present study, our technology also possesses the benefit of being able to produce glucose solutions with concentrations above 100 g/L, while retaining a glucose yield above 70% and operating at high solids loadings (ten times higher compared to Kuo et al.). In general, our process has similarities to that developed by Farone and Cuzens aimed at processing general lignocellulosic biomass, in that both methods are based on two-step, sulfuric-acid-catalyzed, hydrolysis processes, giving comparable results [15]. The notable difference is that the process presented in this study is optimized with regard to saccharifying post-consumer cotton waste textiles. In summary, the inherent resistance toward hydrolysis of cotton textiles was overcome by the exposure to the concentrated sulfuric acid in the pre-hydrolysis step, while the moderate temperature in the post-hydrolysis step allowed for efficient saccharification and prevented by-product formation. Finally, the optimized solids loading in the pre-hydrolysis step and the concentration of sulfuric acid in the post-hydrolysis step resulted in a high glucose yield and a product of high concentration.

Table 1. Reported yields, product concentrations, and raw material solids loadings from studies producing glucose from cellulose and cotton waste textiles, including the present study.

Study	Glucose Yield (%)	Glucose Concentration (G/L)	Solids Loading (Dry G Matter /G Solution)	Raw Material Used
Kong-Win Chang et al. [17]	98	-	0.03	Cellulose from steam-pretreated straw
Sasaki et al. without enzymes [36]	29	-	0.03	Cotton towels
Sasaki et al. with enzymes [36]	78	-	0.02	Cotton towels
Kuo et al. [37]	80	45	0.08	Waste cotton T-shirts
Our previous study [22]	92	3	0.06	Waste cotton bed linens
Present study	72	109	0.74	Waste cotton bed linens

In this study, cotton waste textiles were used as a proxy for general cellulosic waste textiles. This was partly done since it is the most abundant type of waste textiles within the category of cellulosic waste textiles, which means that it accurately represents the majority of said waste category and is comparably easy to collect in larger quantities [6]. Secondly, cellulose found in cotton is harder to hydrolyze compared to cellulose from other cellulosic textiles due to its high degree of polymerization and crystallinity [14,18,22,26]. Furthermore, optimizing the process to overcome this resistance towards hydrolysis exhibited by cotton waste textiles would ensure that the other types of cellulose-based waste textiles could be valorized following the same process. To confirm this assumption, an experiment where the two-step acid hydrolysis process was applied to waste textiles consisting of 100% viscose was conducted. The results show that a yield above 80% could also be achieved from viscose waste, which confirms that the process could be extrapolated to other types of cellulosic waste textiles as well.

In order to provide a viable valorization option to all cellulose-based waste textiles unfit for fiber recycling and fiber regeneration, the process should be able to treat fiber blends, as well as textiles made of only one type of fiber. This is because a large fraction of today's textiles is blended with other fiber types to combine the benefits from different fiber types in a single fabric. Nevertheless, the process proposed in this paper shows promise in this regard as well. Other researchers have shown that it is possible to use sulfuric acid as a separating agent for separating polyester from cellulosic fibers when those are blended in a single fabric. The resistance of polyester to the damaging effect of sulfuric acid allowed the researchers to separate polyester at high recovery rates from blends of polyester and cotton, as well as polyester and rayon [24]. While fabrics where cellulosic fibers are blended with polyester are common, the textile market consists of various fiber blends containing cellulosic fibers and, as such, a more thorough study is needed in order to measure the effectiveness of this process in each of those cases.

3.3. Recyclability of Solid Residue

When the solid residue from a previous treatment cycle of cotton waste textiles (i.e., the filter cake obtained after vacuum filtration) was mixed with fresh cotton waste textiles and processed once more, the overall glucose yield, based on the theoretical content of monosaccharides in the combined material, decreased (Figure 5). Two different values of the glucose yield were calculated: one assuming that the solid residue obtained after vacuum filtration consisted purely of glucan and the other assuming that all the non-cellulosic material present in the raw material was recovered in the solid residue after vacuum filtration, as described in Section 2.6. These assumptions serve as an upper and a lower limit of the oligomeric sugars recovered in the solid residue being recycled. The true glucan content of the solid residue is between these two values, with some non-cellulosic material being recovered in both the solid residue and the liquid fraction after vacuum filtration.

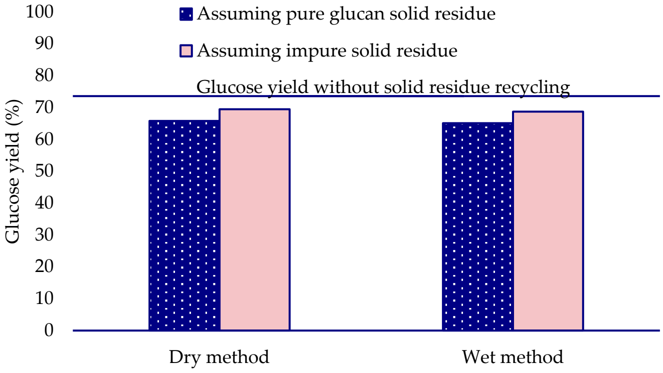

Figure 5. Glucose yield after acid hydrolysis of cotton waste textiles combined with the solid residue from a previous treatment cycle. The two values of the yield were calculated assuming that the solid residue contained non-cellulosic impurities (pink) or not (blue with white dots).

The slight decrease in glucose yield caused by the introduction of solid residue from a previous cycle is likely due to the low reactivity of the recycled solid residue rather than a reduction in overall efficiency. Lower reactivity of the recycled solid residue is supported by the fact that the crystallinity of cellulose can be increased following partial hydrolysis. Sannigrahi et al. [34] showed that partial acid hydrolysis increased the crystallinity of cellulose and attributed this to the fact that the more amorphous regions of the cellulose are hydrolyzed first, effectively concentrating the more crystalline regions in the sample. An alternative explanation could be formation of unknown products during treatment and/or post-processing that reduces the reactivity of the remaining solid residue.

It can be assumed that the degree of hydrolysis of the fresh waste textiles was not negatively affected by the addition of recycled solid residue, as replacing part of the waste textiles with a material with a lower reactivity means the remaining fresh waste textiles experienced less competition for the catalyst. In fact, assuming that the glucose yield from fresh waste textiles remained the same, the glucose yield from the recycled solid residue was 20–30% using the dry method, and 15–25% using the wet method. This illustrates the much lower reactivity of the recycled solid residue than the fresh waste textiles, whose glucose yield was approximately 72%.

In the case of the wet method, the solid residue was not added until the post-hydrolysis step, and since the mass of substrate (waste textiles and recycled solid residue) was chosen so that the ratio of substrate to sulfuric acid was kept at the same level in the post-hydrolysis step between the wet method, the dry method and the original method described in Section 2.2, the solids loading in the pre-hydrolysis step was decreased. As shown in our previous study, a decrease in solids loadings in the pre-hydrolysis step corresponds to an increase in the degree of hydrolysis of the raw material in the process [22]. This implies that the glucose yield of the fresh waste textiles in the wet method could have been higher than assumed, and consequently the values presented on the glucose yield of the recycled solid residue are likely exaggerated and should be regarded as upper limits. This significant decrease in reactivity emphasizes the importance of maximizing the once-through glucose yield of the process, and that the solid residue should be used for other purposes, possibly as a solid fuel, as solid residue from sulfuric-acid-catalyzed hydrolysis of lignocellulosic biomass has been shown to burn well [15].

3.4. Product Requirement and Post-Processing

The glucose produced in this process can be used as a platform chemical for various products. Attractive alternatives include butanediol and caprolactam, which are used to produce spandex and nylon, respectively [38–40]. This is especially attractive since using waste textiles as a raw material for new textile production would keep the value of the waste textiles within the textile value chain, reduce the consumption of virgin raw materials, and reduce waste. Another option is to ferment the glucose into ethanol for biofuel production. Generally, post-processing of glucose involves microbial metabolic conversion, thus the glucose solution must be microbially compatible. It has been reported that the optimal glucose concentration for ethanol production using *Saccharomyces cerevisiae,* a very common microorganism in fermentation, is 55 g/L [41]. *S. cerevisiae* is regarded as a rather robust microorganism, tolerating high glucose concentrations before fermentation is inhibited, while other microorganisms require lower glucose concentrations in order to function optimally. Additionally, since producing products of low concentrations adds to the costs associated with separation and recovery, it is advantageous to produce a concentrated product [42]. This reduces transportation costs, and the product can be readily diluted to target values, such as 55 g/L in the case of bioethanol production. We therefore suggest a minimum concentration of 100 g glucose/L for the product.

There are, however, challenges associated with the purification of the glucose solution. Before any microbial post-processing can take place, the glucose must be separated from the sulfuric acid in the product mixture. This is important not only with respect to microbial compatibility, since the low pH of the solution would prevent any microbial growth, but also with respect to recycling of the sulfuric acid. Without an efficient method of separating and recycling the sulfuric acid, the process would generate large amounts of waste and become unsustainable. The focus of this research has been to study and optimize the parameters in order to achieve a process that produces a concentrated product, while at the same time maintaining a high yield. Consequently, since downstream processing and purification of the product was not included in the focus of this study, separation of the sulfuric acid from the glucose solution remains to be investigated further. Several methods and techniques have been suggested for the separation of sugars from acid-containing hydrolysate of lignocellulosic materials, including ion exclusion chromatography, solvent extraction, electrodialysis, and membrane technology, but further research is needed to determine their applicability in this case [43,44]. However, should the separation prove to be uneconomic, alternative approaches, such as intermediate, partial separation of the sulfuric acid between the pre-hydrolysis step and the post-hydrolysis step using membrane filtration, might help increase feasibility. This would further decrease the water consumption in order to reach the lower concentration of sulfuric acid in the post-hydrolysis step, possibly increasing the glucose concentration even further, without affecting the glucose yield. Ultimately, exchanging the sulfuric acid for enzymes in the post-hydrolysis step would bypass the glucose–acid separation challenge completely. Since pre-hydrolysis left the cotton waste textiles completely de-crystallized, this intermediary material could possibly suit as a perfect substrate for enzymatic hydrolysis, since the problems related to increased apparent crystallinity would be minimized, something that has previously been reported during acidic pretreatment of lignocellulosic biomass prior to enzymatic hydrolysis [34].

4. Conclusions

The proposed process provides a fast and efficient method of transforming cotton waste textiles into glucose, and very likely most cellulose-based waste textiles. The results of the current study show that it is possible to achieve glucose yields above 70% from cotton waste textiles, while exceeding a benchmark for the glucose concentration of 100 g/L, which, to the best of our knowledge, has not yet been reported in the literature. This was achieved while maintaining an optimal, high textile-to-sulfuric acid ratio in the pre-hydrolysis step of 0.74 g dry textiles/g 80 wt.% H_2SO_4, during which the cellulose in the textiles was shown to be completely de-crystallized. An operating temperature of 100 °C in the post-hydrolysis step is superior to both higher and lower temperatures, resulting in both a higher yield and concentration of glucose, due to the significant by-product formation at 121 °C and the low reactivity at 80 °C. Finally, the proposed process does not rely on enzymes and can easily be modified to accommodate different requirements on the product; however, recycling of the sulfuric acid remains an interesting subject for future studies.

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