Chemical recycling of cotton-based waste textiles by sulfuric acid hydrolysis

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Picture on front page: Cotton-based waste textiles. Photo by Edvin Ruuth

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Preface

This master thesis was conducted at the Department of Chemical Engineering at Lund University in the spring of 2020, with the aim of developing a method to chemically recycle cotton-based waste textiles.

The process of writing this master thesis has been very fun and, naturally, also challenging. It would not have been possible without the warm welcome and immense support I have received from all employees at the Department of Chemical Engineering at Lund University, and for this I would like to thank you all. The department has been a very friendly and inviting working environment. Almost wherever I have gone, I have received a helping hand or some kind words of advice, so much that I cannot mention you all by name (however, I can refer to the list of names of the employees of the department) but you should know that I am grateful to you all. However, there are some of you that I would like to take the opportunity to express my gratitude towards in particular. To begin, I would like to thank my supervisor Miguel Sanchis Sebastiá for the immense support he has provided me with. Whenever I needed advice or help of any kind, he always made sure he had time for me, despite having a full schedule of his own. He has provided me with a lot of valuable feedback and advice, not only on my master thesis, but also on matters regarding my future and life in general – thank you! Secondly, I would like to thank Ruben Juárez Cámara and Stina Karlsson for sharing their office with me, providing me with much needed distractions from my work and the occasional, much appreciated, master class in Excel.

I would also like to express my deep gratitude towards all my friends and my family who have supported my throughout not only this project, but also my entire education. My most sincere gratitude goes to my partner Isabell Bågenholm, whose love and support is invaluable to me. Whenever things feel tough, you are there for me.

Finally, I would like to thank *you* for reading this thesis. It brings me joy that someone takes their time to read what I have been spending most of my time with during this spring, I hope you will find it interesting!

May 28th 2020, Lund
Edvin Ruuth

Abstract

Large amounts of waste textiles are produced annually, of which only a small fraction is recycled currently. The purpose of this study was to develop a method to recycle cotton-based waste textiles chemically that can be coupled to the production of biofuels or green chemicals. Bedlinens, labeled 100% cotton, were dissolved and hydrolyzed in sulfuric acid to produce a glucose solution without the need of enzymes. One-step hydrolysis, where dissolution of raw material and hydrolysis occurred at the same conditions, and two-step hydrolysis, where the raw material was dissolved in concentrated sulfuric acid in a first step followed by hydrolysis in diluted sulfuric acid in a second step, were studied. The one-step procedure was not able to deliver high yields nor glucose concentrations due to the limitations of using only one particular concentration of acid. However, the two-step procedure was successful in producing pure, concentrated glucose solutions. When using 5wt% sulfuric acid in the second step, it was possible to obtain a 40 g/L solution and a yield of 84%, while increasing the concentration of sulfuric acid to 7.5% in the second step allowed to reach a higher glucose concentration of 50 g/L, but at a lower yield (68%). It could be expected that the solutions can be easily fermented to fuels or chemicals, as there are almost no impurities due to by-production formation. Further studies are needed to assess the economic viability of this process on a commercial scale, although it stands in a good position to compete with lignocellulose-based processes thanks to the cost savings in feedstock and enzymes.

Sammanfattning

Varje år produceras stora mängder avfallstextilier av vilka endast en bråkdel återvinns. Syftet med den här studien var att utveckla en metod för att kemiskt återvinna kasserade bomullstextilier. Syftet var att metoden i den här studien skulle gå att koppla till produktion av biobränslen och gröna kemikalier. Sängkläder, märkta 100% bomull, löstes upp och hydrolyserades i svavelsyra för att producera en glukoslösning utan att använda enzymer. En-stegshydrolys, där upplösning av råmaterial och hydrolys ägde rum vid samma förutsättningar, och två-stegshydrolys, där råmaterialet upplöstes i koncentrerad svavelsyra i ett första steg, följt av hydrolys i utspädd svavelsyra i ett andra steg, studerades. En-stegshydrolysen lyckades varken uppnå högt utbyte av glukos eller höga glukoskoncentrationer på grund av begränsningarna av att bara använda en konstant halt av svavelsyra genom hela försöken. Två-stegshydrolysen var emellertid framgångsrik i att producera en ren, koncentrerad glukoslösning. När 5% svavelsyra användes i det andra steget var det möjligt att nå en koncentration av glukos på 40 g/L till ett utbyte av 84%, medan en ökning av koncentrationen på svavelsyran i det andra steget till 7.5% möjliggjorde en högre koncentration av glukos på 50 g/L, men med ett lägre utbyte på 68%. De resulterande sockerlösningarna förväntas vara enkla att jäsa för vidare produktion av biobränslen och kemikalier eftersom det finns nästan inga förorenande biprodukter närvarande. Vidare studier behövs för att undersöka den ekonomiska genomförbarheten av den här processen på en kommersiell skala, men den har en bra utgångspunkt för att konkurrera med lignocellulosabaserade processer tack vare kostnadsbesparingar inom råmaterial och avsaknaden av enzymer.

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1. Introduction

1.1. Waste generation and the environment

The environment is under a lot of pressure caused by human activity. We consume excessively at ever increasing rates and we release unacceptable amounts of harmful waste and substances to the environment at the same time. Earth Overshoot Day, the day when humanity has exhausted all biological resources the earth can renew during a full year, is occurring earlier than ever according to the Global Footprint Network (Global Footprint Network, 2020). Due to this exhaustion of natural resources occurring earlier and earlier in the year, it is very important that humanity starts consuming less and more responsibly. We must develop more sustainable production processes and decrease the amount of emissions to the environment. One method of doing this would be to utilize waste as feedstock for other processes.

1.1.1. Waste textile generation

One stream of solid waste that is generated in large amounts every year is waste textiles. An increasing global population, together with an increasing demand of textiles per capita, has led to a dramatic increase in the production of textiles. The human population has more than tripled since 1950 (Roser et al., 2020), when the worldwide consumption of textiles was 3.7 kg per capita. In 2007, the worldwide consumption of textiles had increased to 11.1 kg per capita (Pensupa et al., 2017). With both the human population and the textile consumption per capita having increased more than three-fold each, this means that the total textile production has increased more than nine times compared to that of 1950. Textiles cannot be used indefinitely and have to be discarded sooner or later, for this reason, the massive annual production of textiles leads to a very large amount of waste textiles being produced every year. In Sweden, the consumption of textiles is 22 kg per person per year and the produced textile waste is mostly sent to incineration with energy recovery or landfill, like in most other countries (Pensupa et al., 2017, Peters et al., 2019).

1.1.2. Waste textile management

The waste management hierarchy states that reusing is more beneficial than recycling of materials. Reusing means that a discarded item of textile is used again, for example textiles bought on the second-hand market. Recycling, converting waste material into new materials and products, is in turn favorable over incineration with energy recovery which is still better than landfilling (Zamani et al., 2014). Reusing of discarded textiles is not possible when the fabric is too damaged, but it can usually still be used to recycle the materials of the fabric. Despite reusing and recycling being more beneficial than incineration and landfilling, most textile waste is currently incinerated or sent to landfill, which means there is ample room for more and better recycling methods, which the textile industry could benefit greatly from. One challenge when it comes to textile recycling, is that use and laundering shortens both the fiber length and the degree of polymerization of the polymer chains in the fabric. Because of these damages, mechanical recycling of textiles, where the fibers are separated and turned into new fabric, is limited, however, it is yet still the most common form of textile recycling, because there are no better commercial alternatives, at the moment (Peters et al., 2019).

1.2. The energy sector and the environment

Just as the generation of waste textiles and other solid wastes is problematic for the global environment, so are emissions of greenhouse gases, which originate first and foremost from the usage of fossil fuels in the global energy sector.

1.2.1. Energy consumption

In 2017 the total energy consumption in Sweden was 573 TWh. The Swedish energy consumption is divided between three user sectors: the industrial sector, the residential and service sector and the transport sector. Out of the three user sectors, the industrial and the residential and service sectors mainly uses biofuel and electricity, which is mainly generated from renewable sources, but the transport sector mainly uses petroleum-based products. In 2017 the transport sector used 88 TWh. Out of that, 66 TWh originated from petroleum products while only 19 TWh originated from biofuels (Energimyndigheten, 2019). For these reasons, the transport sector is the sector that could improve the most when it comes to environmental impact, as it consumes such a large share of fossil fuels. A large and cheap supply of biofuels could drastically improve the carbon footprint of the transport sector.

1.2.2. Lignocellulose for biofuel production

Ethanol has for some time been considered a promising alternative to petroleum-based fuels, but it still suffers from being comparatively expensive and, in the case of first generation ethanol, its production competes for limited agricultural land that could otherwise be utilized for much needed food and feed production (Folkesson et al., 2019, Sun and Cheng, 2002). A cheap and abundant alternative feedstock for ethanol production could solve these problems and because of that lignocellulosic materials have been considered. Lignocellulosic material is found in crop residues, grass and wood for example and typically consists of a mixture of cellulose, hemicellulose and lignin (McMillan, 1994, Sun and Cheng, 2002). One of the primary pathways that have been investigated is hydrolysis of the cellulose content, in lignocellulose, to reducing sugars with the help of enzymes followed by subsequent fermentation of said sugars to ethanol (Sun and Cheng, 2002). To improve this process, removal of hemicellulose and lignin together with decrystallization of the cellulose has been showed to be very efficient (McMillan, 1994). Thus, to achieve better results, it is common to apply a pretreatment process of lignocellulosic material before hydrolysis. However, one large bottleneck when it comes to utilize lignocellulosic material in biorefineries is that large quantities of hydrolase enzymes are needed, which are expensive (Jiménez-Sánchez and Philp, 2016).

1.3. Biofuels from waste textiles

A possible solution for the problems of accumulating amounts of solid wastes and overconsumption of fossil fuels is to produce biofuels from waste textiles. A large portion of waste textiles produced today is cotton fabrics, which mainly consists of cellulose and as such biofuel production from waste textiles is promising.

1.3.1. Cotton-based textile waste for ethanol production

Cotton contains almost pure cellulose with a high degree of crystallinity without any lignin or hemicellulose (Jeihanipour and Taherzadeh, 2009, McCall and Jurgens, 1951, Mitchell et al., 2005). Thus, cotton has a great advantage over generic lignocellulosic material as it does not have to be pretreated to remove lignin and hemicellulose. This advantage has brought attention to possible processing of cotton-based waste textiles as a feedstock for ethanol production.

However, the high degree of crystallinity of cotton does limit the efficiency of enzymatic hydrolysis. In addition, cotton textiles contain elements that are not present in natural cotton. For instance, there are zippers, buttons and seams that are made of other materials that have to be removed to get a pure cotton waste textile stream. Furthermore, textiles are typically dyed, and studies have shown that some dyeing chemicals do not significantly affect enzymatic hydrolysis of textiles or the subsequent fermentation process, while other dyeing chemicals hinder the process, depending on their chemistry (Kuo et al., 2014, Czilik et al., 2002). Fabrics can also be made with more than one kind of fibers, but other studies have found that the presence of other fibers in the textile does not inhibit acidic hydrolysis, with the yield of reducing sugars being comparable to the cotton fraction in the textile blend, and that treating the textile with acid can separate cotton fibers from polyester fibers (Kuo et al., 2014, Ouchi et al., 2010, Shen et al., 2013).

Many researchers have investigated the possibility of, and tried developing, a process to convert cotton to ethanol using enzymatic hydrolysis, with some sort of pretreatment - usually acidic or alkaline - followed by fermentation (Jeihanipour et al., 2010, Jeihanipour and Taherzadeh, 2009, Kuo et al., 2014, Shen et al., 2013). Another option is to conduct the hydrolysis chemically, which has the advantage that enzymes are no longer needed. Previous research has shown that it is possible to hydrolyze pure cellulose using acid (Chu et al., 2011). Furthermore, there has also been studies in which sulfuric acid was used to hydrolyze cotton textiles, albeit within a very narrow span of operating conditions (Sasaki et al., 2019a, Sasaki et al., 2019b). To the best of our knowledge, it seems that no one has thoroughly investigated the possibility of developing such a process by studying the impact of different operating conditions and subsequently optimizing and upscaling the process.

The purpose of this study is to develop a method of producing glucose, that can be used to produce biofuels or other green chemicals, from pure cotton textile waste. For this purpose, acid hydrolysis was employed, using sulfuric acid as the sole catalyst for the hydrolysis of cellulose to reducing sugars. The idea is that the process in this study would be an environmentally friendly and economic alternative to current management strategies of waste textiles. Based on the abundance of waste textiles, the feedstock would be cheap and plentiful, further enhancing the economic viability of the proposed process. Also, the process is not sensitive to the condition of the fibers, since it does not rely on mechanical recycling of the fibers, so all kinds of cotton-textile could in theory be useful. Finally, studies indicate that such a process could also be rather robust, capable of processing a feedstock of varying quality and composition.

2. Methods

2.1. Raw material

The waste textile used in this work was used and discarded bedlinens labelled 100 % cotton, sourced from the author's home, the homes of employees at the Department of Chemical Engineering at Lund University and in collaboration with Human Bridge, an organization that collects waste textile in Sweden. Only textiles that had been deemed unfit for reselling were chosen for the study. Labels, seams and buttons were removed from the bedlinens and the cloth was cut into pieces, approximately 15 mm by 15 mm, using a textile knife (Figure 1). The pieces of textile were mixed thoroughly prior to the experiments.

Figure 1. Raw material after size reduction.

2.2. Acid hydrolysis experiments

2.2.1. One-step acid hydrolysis

One-step acid hydrolysis experiments were performed by exposing approximately 42 g of waste textiles to 760 g of sulfuric acid, in a one-liter blue cap bottle, at different temperatures and residence times, according to Table 1. The sulfuric acid was prepared through diluting concentrated sulfuric acid (95wt%) to the concentrations specified in Table 1. The experiments at 130 °C were performed in an autoclave, while the rest were performed in a water bath. After the completion of the hydrolysis, the content of the bottles were vacuum filtered through a 100 µm filter cloth, generating a liquid fraction and a residual solid fraction that were subjected to further analysis.

Table 1. Conditions of each of the one-step acid hydrolysis experiments.

Experiment	Temperature (°C)	Residence time (h)	[H_2SO_4] (%wt)
1	130	6	60
2	130	6	5
3	130	1	60
4	130	1	5
5	30	6	60
6	30	6	5
7	30	1	60
8	30	1	5
9	80	3.5	5
10	80	3.5	60
11	80	6	32.5
12	80	1	32.5
13	130	3.5	32.5
14	30	3.5	32.5
15	80	3.5	32.5
16	80	3.5	32.5

2.2.2. Two-step acid hydrolysis

Two-step acid hydrolysis experiments were performed by first exposing approximately 16 g of waste textiles to 285 g of sulfuric acid, in a 500 ml blue cap bottle, at different temperatures and residence times according to Table 2. The sulfuric acid for this first step was prepared by diluting concentrated sulfuric acid (95wt%) to the concentrations specified in Table 2. Secondly, after the completion of the residence time, the mixture was diluted in a five-liter blue cap bottle until it reached a concentration of 5wt% sulfuric acid and exposed to 121 °C for one hour. The first hydrolysis step of the experiments was performed in a water bath while the second hydrolysis step of the experiments was performed in an autoclave. After the completion of the two-step hydrolysis, the suspension was vacuum filtered through a 20 µm filter paper, generating a liquid fraction and a residual solid fraction that were subjected to further analysis.

Table 2. Conditions of the first step for each of the two-step acid hydrolysis experiments.

Experiment	[H_2SO_4] in first step (wt%)	Temperature (°C)	Residence time (h)
17	60	80	3.5
18	72	30	1
19	65	30	1
20	60	30	1
21	80	30	1
22	65	80	3.5

2.2.3. Modifications of the procedure to further increase solids loading

Additional two-step hydrolysis experiments (experiment 23 through 29) were conducted, in which the solids loading in the first step was gradually increased from 0.16 g dry textiles/g sulfuric acid solution to 1.12 g dry textile/g sulfuric acid. All the experiments were performed with 80% sulfuric acid, except one (at 0.67 g dry textiles/g sulfuric acid solution) which was performed with 72% sulfuric acid as well. The rest of the procedure was the same as explained in Section 2.2.2, with the temperature in the first step being 30 °C.

Experiments 28 and 29 were conducted in a fed-batch manner where the material was fed progressively in the first step. In experiment 28, one fourth of the material was fed every 15 minutes, while in experiment 29, half of the material was fed initially and, after 20 min, each of the remaining fourths were fed every 20 min.

Two more experiments, experiments 30 and 31, were conducted, in which the sulfuric acid in the second step was increased to 7.5wt% and the solids loadings in the first step were 0.73 g dry textiles/g sulfuric acid solution and 0.53 g dry textiles/g sulfuric acid solution, respectively. The concentration of sulfuric acid in the first step was 80% and the temperature, 30 °C.

2.3. Analysis

2.3.1. Raw material analysis

The raw material was analyzed for total solids and cellulose content. The content of total solids was determined by drying the samples in an oven at 105 °C according to the National Renewable Energy Laboratory (NREL) procedure "Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples" (Sluiter et al., 2008a). The cellulose content was measured by acid hydrolyzing samples of waste textile and measuring the resulting glucose via High Performance Liquid Chromatography (HPLC) according to the procedure "Determination of Structural Carbohydrates and Lignin in Biomass" developed by NREL (Sluiter et al., 2008b).

2.3.2. Analysis of samples from acid hydrolysis experiments

Samples were taken from the liquid fraction and kept in a freezer until analyzed according to the NREL Procedure "HPLC Analysis of Liquid Fractions of Process Samples for Monomeric Sugars and Cellobiose" (Ruiz and Ehrman, 1996).

The total solids content of the residual solid was measured by drying samples at 105 °C following the NREL Procedure "Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples" (Sluiter et al., 2008a). Samples were also weighed, washed and dried to measure the water insoluble solids content according to the procedure "Determination of Insoluble Solids in Pretreated Biomass Material" by NREL (Sluiter et al., 2008c).

2.3.3. Calculations

The glucose yield from the hydrolysis was calculated as the mass of glucose produced divided by the total mass equivalent of cellulose present in the sample before treatment, adjusted for the mass difference between glucose and glucan (Equation 1).

$$Y_{glucose} = c_{glucose} \cdot \frac{V}{m_{dry\ textiles} \cdot \eta_{cellulose} \cdot 1.11} \tag{1}$$

where $Y_{glucose}$ represents the glucose yield, $c_{glucose}$ the concentration of glucose in the liquid fraction after the acid hydrolysis experiment, V the volume of the liquid fraction, $m_{dry\ textiles}$ the dry mass of textiles used in the experiment, $\eta_{cellulose}$ the content of cellulose in the raw material and 1.11 the factor to convert the mass of cellulose to the equivalent mass of glucose.

The solid recovery was calculated as the mass of water insoluble solids after treatment divided by the dry total mass of the solid raw material before the treatment (Equation 2).

$$\eta_{SR} = \frac{m_{solids} \cdot \eta_{TS} \cdot \eta_{WIS}}{m_{dry\ textiles}} \tag{2}$$

where η_{SR} is the solid recovery, m_{solids} the mass of wet solids in the retentate after filtration, η_{TS} the fraction of total solids in the wet retentate and η_{WIS} the fraction of water insoluble solids of the total solids.

Glucose losses were calculated as the mass of glucose that degraded to form hydroxymethylfurfural (HMF) and levulinic acid (LevH) divided by the total mass equivalent of cellulose in the sample before treatment, adjusted for mass difference between glucose and glucan (Equation 3-5).

$$\eta_{GL} = \frac{m_{GtLevH} + m_{GtHMF}}{m_{dry\ textiles} \cdot \eta_{cellulose} \cdot 1.11} \tag{3}$$

$$m_{GtLevH} = \frac{c_{LevH} \cdot V \cdot M_{glucose}}{M_{LevH}} \tag{4}$$

$$m_{GtHMF} = \frac{c_{HMF} \cdot V \cdot M_{glucose}}{M_{HMF}} \tag{5}$$

where η_{GL} represents the glucose losses, m_{GtLevH} the mass of glucose that reacted to form LevH, m_{GtHMF} the mass of glucose that reacted to form HMF, c_{LevH} the concentration of LevH in the liquid product fraction, $M_{glucose}$ the molar mass of glucose, M_{LevH} the molar mass of LevH, c_{HMF} the concentration of HMF in the liquid product fraction and M_{HMF} the molar mass of HMF.

The degree of hydrolysis was calculated as the mass of glucose formed and degraded during treatment divided by the mass of dissolved cellulose, adjusted for the mass difference between glucose and glucan (Equation 6).

$$\eta_{DoH} = \frac{c_{glucose} \cdot V + m_{GtLevH} + m_{GtHMF}}{(1 - \eta_{SR}) \cdot m_{dry\ textiles} \cdot 1.11} \tag{6}$$

3. Results and Discussion

3.1. Raw material composition

The raw material analysis in this study showed that the textiles had a total solids content of 95.1wt%, standard deviation of 0.8wt%, and a cellulose content of 93.0wt% on a dry basis, standard deviation of 0.7wt%. Pure cotton typically consists of 94% cellulose on a dry basis (McCall and Jurgens, 1951). When cotton is treated and turned into textiles the content of cellulose is first increased due to scouring and bleaching and then decreased when dyes and other additives are added, giving pure cotton cloth a high content of cellulose, albeit not 100% (Kuo et al., 2014, Miranda et al., 2007, Mitchell et al., 2005). Considering this, the results from the raw material analysis are considered to be sufficiently accurate.

3.2. One-step acid hydrolysis

3.2.1. Glucose yield

The glucose yield was low for all experiments: the highest yield achieved was 17.5% and several settings showed no measurable yield at all (Figure 2). However, the reason why the yield is comparatively low for all settings is caused by two different phenomena – poor dissolution of the material and glucose degradation to HMF or organic acids.

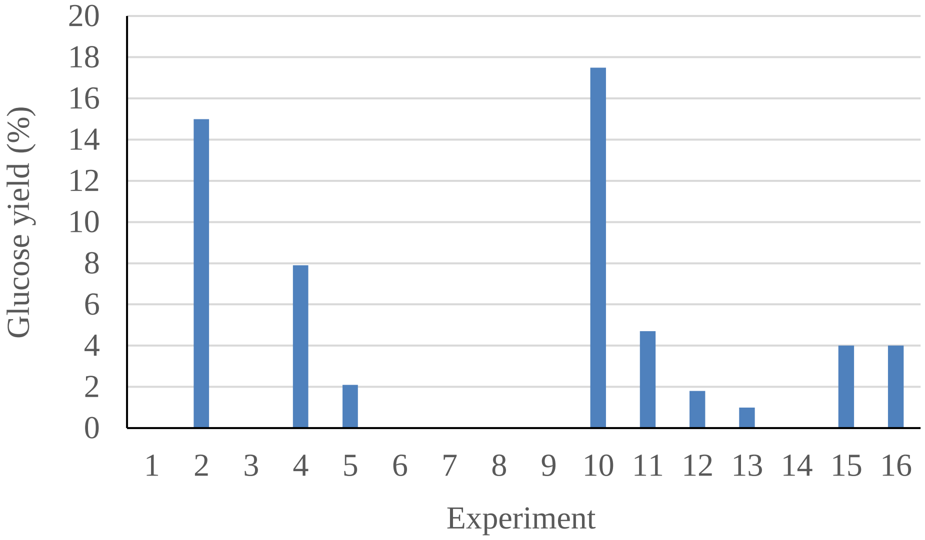

Figure 2. Glucose yield from the one-step acid hydrolysis analysis.

3.2.2. Solid recovery and glucose losses

The analysis of the samples provided an estimate of the amount of the original material that did not dissolve (solid recovery) and the amount of formed glucose that degraded into other derivatives, such as HMF and levulinic acid (glucose losses). Two models were fitted to the data through linear regression, one for solid recovery and one for glucose losses, to evaluate their behavior at various operating conditions. Using the models several sets of response surfaces were constructed. Figures 3, 4 and 5 show the variation of the solid recovery (left) and the glucose losses (right) across different values for the residence time and temperature for 5%, 32.5% and 60% sulfuric acid, respectively.

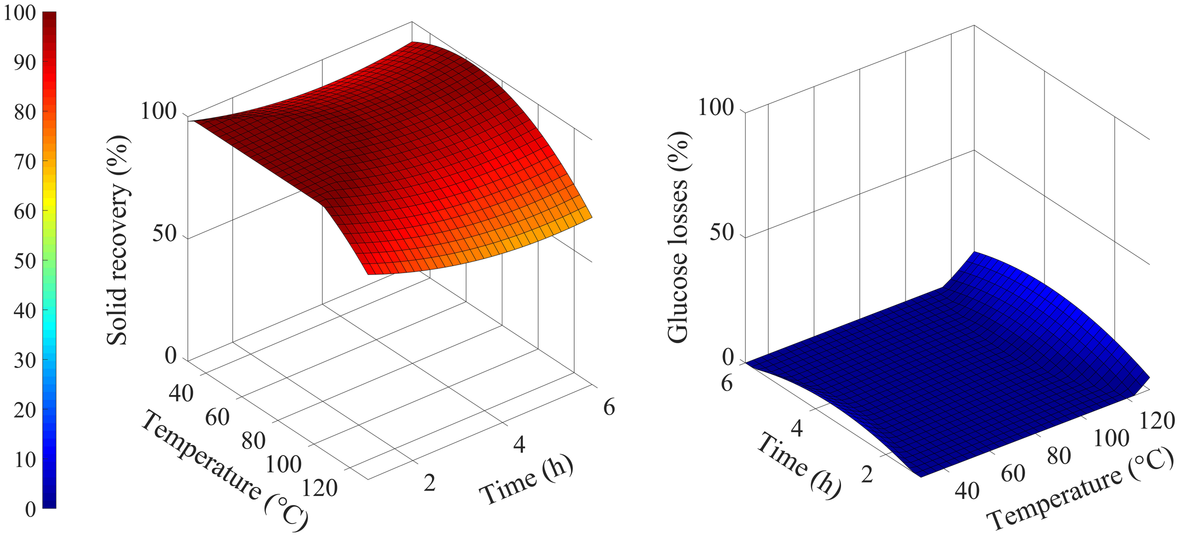

Figure 3. Response surfaces for solid recovery (left) and glucose losses (right) at 5% sulfuric acid.

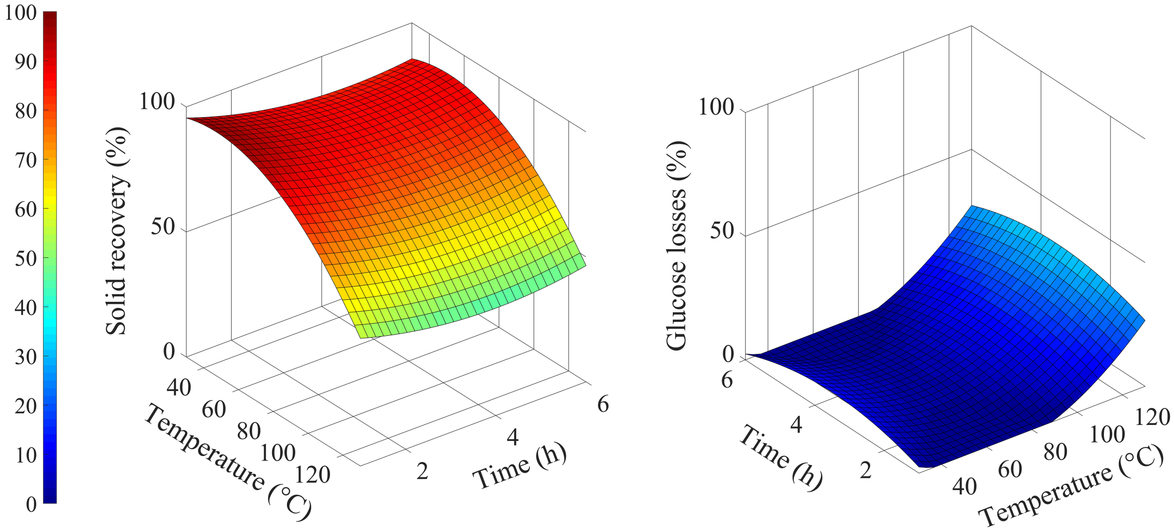

Figure 4. Response surfaces for solid recovery (left) and glucose losses (right) at 32.5% sulfuric acid.

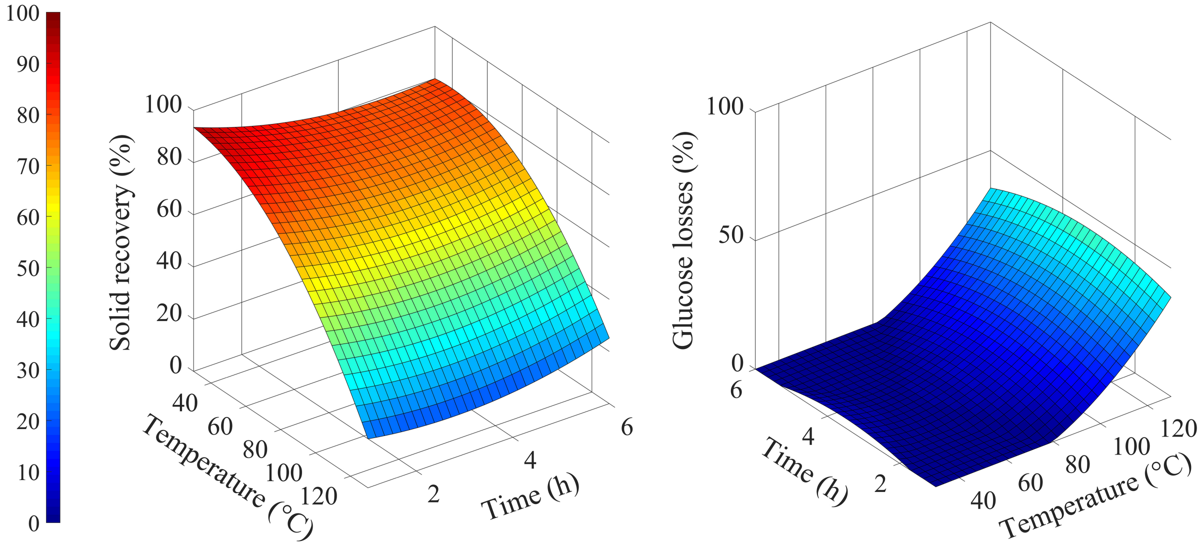

Figure 5. Response surfaces for solid recovery (left) and glucose losses (right) at 60% sulfuric acid.

As can be seen when studying the response surfaces in Figures 3-5, the magnitude of the solid recovery and the glucose losses varies over the operating parameters. Both solid recovery and glucose losses have a negative effect on the glucose yield. A high solid recovery means that a low fraction of material has been dissolved for subsequent hydrolysis and a high value of glucose losses means a high fraction of the formed glucose has degraded to other derivatives. Moreover, the two effects seem to complement each other, i.e. when the solid recovery is low, the glucose losses are significant and vice versa, which explains the constant low glucose yield.

3.2.3. Effect of operating parameters on solid recovery

Looking at the response surfaces for solid recovery, Figures 3-5 (left), it is possible to see that there is significant variation in response as the operating parameters vary. The solid recovery decreases slightly as the residence time is prolonged and the effect levels off as the time approaches the end of the temperature range. The effect of decreased solid recovery with increasing residence time was most evident at low temperatures and was hard to detect at high temperatures. For low acid concentration and low to intermediate temperatures, the solid recovery remained at 100% when the residence time was kept short. As the concentration was increased, the effect of the residence time on the solid recovery increased.

The effect of the temperature on the system is more significant than that of the residence time. For low temperatures the solid recovery remained relatively high throughout all times and concentrations but decreased drastically as the temperature increased. This drastic decrease became more evident at higher concentrations of sulfuric acid. For weak and intermediate acid concentrations (5% and 32.5%), the response surfaces for solid recovery exhibit a plateau-like shape at low temperatures. This plateau is larger, i.e. spreads across a larger temperature interval, for weak acid than for intermediate acid as the solid recovery starts to decrease around 70 °C when using intermediate acid compared to around 100 °C for weak acid. The tendency to form a plateau is not present in the respective response surface for strong acid (60%) where the response surface takes the shape of a constant decrease instead. This means that, as the concentration increases, the decrease in solid recovery starts at a lower temperature.

The overall solid recovery decreases as the concentration of sulfuric acid is increased. Furthermore, the concentration of sulfuric acid amplifies the effect of the other parameters on the solid recovery as well. An increase in residence time leads to a larger decrease in solid recovery in strong acid compared to weak acid. The same effect is seen with regards to temperature. The solid recovery decreases the more severe the operating conditions are (high temperature and high concentration of acid), which was anticipated.

3.2.4. Effects of operating conditions on glucose losses

The glucose losses are also varying with varying operating conditions. The residence time have a smaller impact on the glucose losses than it has on the solid recovery. There is a slight curvature of the surface as the residence time progresses leading to a maximum at intermediate residence time for every temperature except for weak acid, where the surface is mostly flat.

The temperature has a much higher impact on the glucose losses compared to the residence time, just as was the case with solid recovery. For low temperatures the glucose losses remained almost non-existent, but as the system reached high temperatures the glucose losses were increased drastically. The temperature after which this effect occurs becomes lower as the acid concentration increases leading to a higher maximum value of the glucose losses with increasing acid concentration. However, the rate at which the glucose losses increase with increasing temperature is similar for varying concentrations of sulfuric acid.

Similar to the behavior of solid recovery, the concentration of sulfuric acid mostly amplifies the effect of the other parameters on the glucose losses. Since the residence time barely affects the system, this amplification from the acid is not evident but the effect of the temperature is greatly increased.

3.2.5. Combined effects of operating conditions on glucose yield

As severity increases, solid recovery decreases and glucose losses increase. Thus, both high severity and low severity display properties that are beneficial for reaching a high glucose yield. Since the residence time shows a small effect on the solid recovery but little to no effect on the glucose losses, intermediate residence times are best suited for dissolving the material while short residence times suffice to limit glucose degradation. High temperatures are best suited for dissolution, but low temperatures are preferred to limit glucose losses. Finally, high concentrations of sulfuric acid display potent dissolution properties but at the same time cause higher degradation.

Through studying the glucose yield and comparing it to the solid recovery for the different experiments, it is clear that, while the glucose yield was low for weak acid, the glucose yield from dissolved material was relatively high compared to strong acid. The dissolution was higher at concentrated acid but the ratio of hydrolyzed material to dissolved material, the degree of hydrolysis, was lower than that for weak acid. Thus, even though weak acid shows little dissolving and degrading properties, it is still potent at hydrolyzing dissolved material.

Since solid recovery exhibits its minimum when glucose losses exhibit their maximum, maximizing the glucose yield in a one-step hydrolysis becomes a matter of compromise between byproduct generation and underutilization of the raw material. A promising alternative to a one-step hydrolysis is therefore a two-step hydrolysis where the dissolving properties of strong acid are utilized, followed by treatment in weak acid where the low degradation and high degree of hydrolysis caused by the weak acid are utilized.

3.2.6. Model validity

The R^2-values for the fitted models were 0.88 and 0.87 for solid recovery and glucose losses, respectively. There are differences for both models between the predictions and the experimental data and they most likely stem from the models not being a perfect fit to the system. With R^2-values of 0.88 and 0.87, respectively, there is room for errors. However, these deviations are deemed to be sufficiently small so that the models can be trusted and depict comprehensive trends of the system.

3.3. Two-step acid hydrolysis

Following the results from the one-step hydrolysis experiments, a two-step hydrolysis treatment of the material was tested. Since the proposed method follows the same pattern as the procedure "Determination of Structural Carbohydrates and Lignin in Biomass" developed by NREL (Sluiter et al., 2008b), treatments based on its operating conditions with varying concentrations of sulfuric acid in the first step were tested.

3.3.1. Glucose yield

The glucose production of the two-step acid hydrolysis was significantly higher than that of the one-step hydrolysis. The glucose yield increased drastically when the concentration of sulfuric acid was increased beyond 60% in the first step, from below quantification limit to above 90% glucose yield at 80% sulfuric acid (Figure 6).

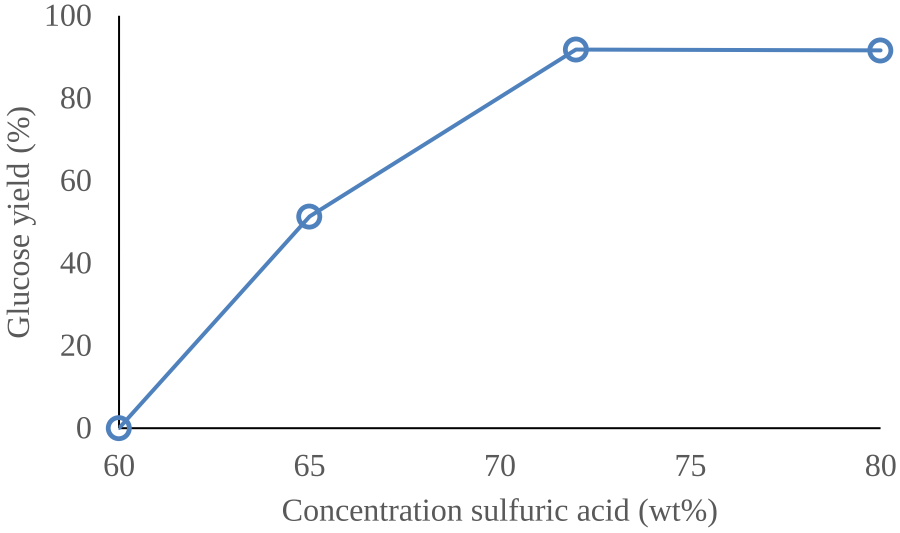

Figure 6. Glucose yield after completed two-step hydrolysis with varying sulfuric acid concentration in the first hydrolysis step at 30°C.

3.3.2. Dissolution of raw material

Similarly to the one-step hydrolysis experiments, the glucose yield depends on several factors. There is a significant increase in dissolution of raw material (raw material that through hydrolysis is broken down into water soluble components e.g. short chains of glucose) as the concentration of sulfuric acid in the dissolution step is increased (Figure 7). The change was most significant between 60% and 65% and the dissolution levelled out as the concentration was increased to 80%, where practically 100% of the raw material was dissolved. The more material is dissolved, the easier it is for the acid to further hydrolyze the cellulose into glucose and this is partly why the yield increases as the concentration of the acid increases in the dissolution step.

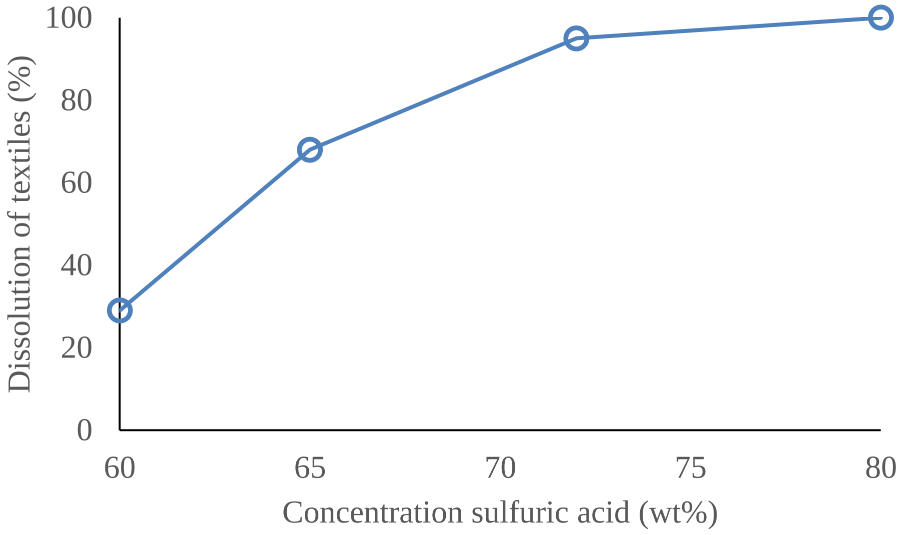

Figure 7. The dissolution of raw material for different concentrations of sulfuric acid in the first step of the hydrolysis.

3.3.3. Degree of hydrolysis

Another factor that affects the glucose yield is the degree of hydrolysis - the fraction of the dissolved material that hydrolyzes further into glucose or any glucose derivatives. Similarly to the dissolution, the degree of hydrolysis became larger as the concentration increased from 60% and levelled out around 72% sulfuric acid (Figure 8). There was a slight decrease in the degree of hydrolysis for 80% sulfuric acid, but that probably stems from the dissolving properties of the concentrated acid. At 80% sulfuric acid all raw material was dissolved, even that which is not cellulose, and thus the degree of hydrolysis is underestimated. If only the dissolved mass of glucan is considered, the degree of hydrolysis at 80% sulfuric acid becomes 91.5%, which is very similar and slightly higher than the degree of hydrolysis at 72% acid.

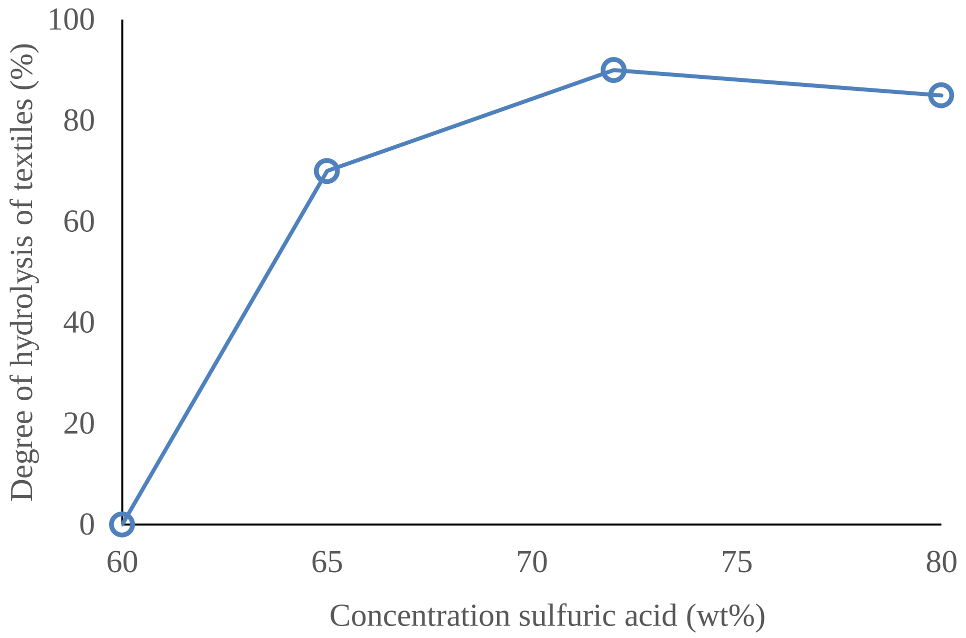

Figure 8. The degree of hydrolysis of the material, after completed two-step hydrolysis, for different concentrations of sulfuric acid in the first step, at 30°C.

In the results from the one-step hydrolysis and the two-step hydrolysis there is a tendency of inhibition of further hydrolysis in samples that have been treated with 60% sulfuric acid. The degree of hydrolysis was significantly lower when the raw material was treated with 60% sulfuric acid compared to all other tested concentrations (5%, 32.5%, 65%, 72% and 80%) at the same conditions. Furthermore, samples treated in 60% sulfuric acid exhibited an inability to produce more glucose through further treatment in 5% sulfuric acid (data not shown). This behavior was not observed for any other concentration of sulfuric acid other than 60%.

Increasing the temperature in the dissolution step yields an improved glucose yield when using 60 % sulfuric acid but a decrease in glucose yield when using 65 % sulfuric acid (Table 3). The degree of hydrolysis for 60% sulfuric acid, while remaining lower than that for 65% sulfuric acid, was increased when the temperature of the dissolution step was increased, something that did not occur for 65% sulfuric acid. This indicates that the inhibitory effect is caused by the concentration of acid and no other parameters of the process, such as temperature or residence time.

Table 3. The table shows the glucose yield and degree of hydrolysis for the double step hydrolysis with varying temperature in the dissolution step.

Concentration sulfuric acid (wt%)	Temperature (°C)	Glucose yield (%)	Degree of hydrolysis (%)
60	30	0	0
60	80	21.7	38
65	30	51.3	70
65	80	28.4	67

3.3.4. Glucose losses

At a temperature of 30°C there was no detectable degradation for any concentration of sulfuric acid in the dissolution step. When comparing the degradation at elevated temperatures for 60% and 65% sulfuric acid in the dissolution step, there was 19% degradation for 65% sulfuric acid while no quantifiable degradation was registered for 60% sulfuric acid. This explains why the glucose yield decreased when the temperature was increased while using 65% sulfuric acid in the dissolution step.

3.4. Increasing solids loading

3.4.1. Concentration of sulfuric acid in the dissolution step

At low solids loading there is almost no difference in performance when using 80% sulfuric acid over 72% in the dissolution step: the glucose yield, the dissolution of the material and the degree of hydrolysis all were very similar. However, 80% acid exhibited slightly higher dissolving properties, dissolving all of the raw material as opposed to 95% dissolved material for 72% sulfuric acid. On the other hand, using 80% sulfuric acid requires to add more water in the second step of the process compared to when using 72% acid. Thus, both 72% and 80% showed attractive properties at low solids loadings and are therefore suitable candidates for experiments at increased solids loading.

However, the difference in performance at different concentrations of sulfuric acid in the dissolution step became much larger at high solids loadings (approximately 7-8 times higher than the one used in the NREL procedure). The most concentrated acid (80%) dissolved the material into a thick, viscous, black syrup while 72% sulfuric acid turned the material into a grey, fibrous paste. The glucose yield was 84% when using 80% acid and 51% when using 72% acid. These results show that at high solids loading, 80% sulfuric acid performed significantly better because of its greater dissolving properties and therefore it was the chosen concentration to perform the subsequent experiments.

3.4.2. Batch experiments at different solids loading

As the solids loading increased, the glucose concentration in the liquid product increased steadily until the solids loading reached 0.74 g dry textiles/g acid, after which it started to decrease (Figure 9). This is because the glucose yield remained above 80%, with only a slight decrease with increasing solids loading, until the solids loading reached 0.74 g dry textiles/g acid. After this point, the glucose yield started to decrease significantly when the solids loading was increased further (Figure 9).

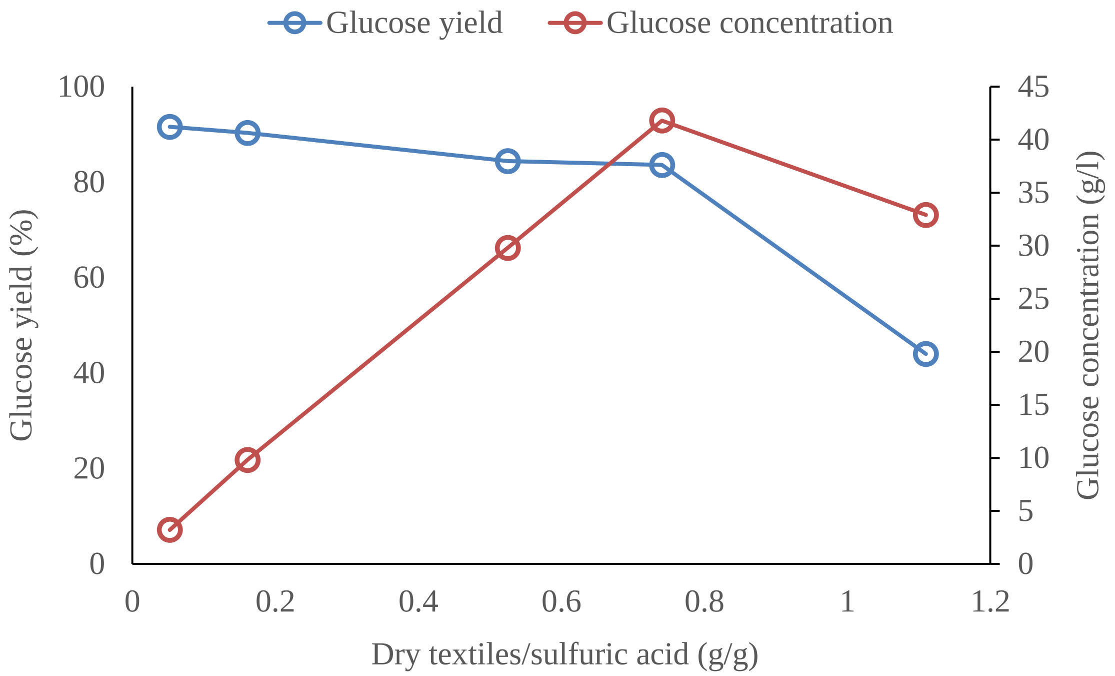

Figure 9. Glucose yield and concentration at different solids loading in the first step of a two-step acid hydrolysis.

The more textile that was added to the sulfuric acid, the more time and mixing was required for the mixture to form a black, viscous fluid (Figure 10). When attempting to perform the experiment at 1.11 g dry textiles/g acid, it did not form a homogeneous syrup but a sticky and very viscous mixture of dissolved, partially dissolved and undissolved textile that required a great torque to mix (Figure 11). A mixture such as the one in Figure 11 has significantly higher mass- and heat transfer resistances compared to the fluid in Figure 10 and it is these resistances that are likely to cause the low glucose yield when the solids loading reach a very high value.

Figure 10. Textiles dissolved in 80% sulfuric acid.

Figure 11. A mixture of dissolved, partially dissolved and undissolved textiles in 80% sulfuric acid.

In a batch procedure, the performance of the process remained approximately the same until a solids loading of 0.75 g dry textiles/g acid was reached, after which both glucose yield and glucose concentration started to decrease significantly. This limit, however, was high enough that it was possible to produce a concentrated glucose solution (42 g/L) coupled with a high glucose yield (84%). Furthermore, there was no evidence of any significant degradation of the material for any setting of solids loading tested, resulting in a pure product.

3.4.3. Modifications of the procedure to further increase solids loading

If glucose concentrations higher than 40 g/L are desired, the procedure needs to be modified. Several modifications were tested: fed-batch procedure in the first step and decreased dilution in the second step.

Using a fed-batch setup in the dissolution step resulted in slightly increased glucose yield and increased glucose concentration. The method helped decrease the effect of low dissolution of the raw material in the dissolution step, but only to some extent. For solids loading of 1.11 g dry textiles/g acid, a batch-wise setup of the dissolution step resulted in a glucose yield of 44% and a glucose concentration of 33 g/L, while two different fed-batch strategies increased the glucose yield and concentration to approximately 50% and 40 g/L, respectively. This indicates that it is possible to improve the glucose production by applying a fed-batch setup in the dissolution step, at very high solids loading.

However, the effect of using a fed-batch strategy is less significant at low solids loadings. At a lower solids loading of 0.74 g dry textiles/g acid, a fed-batch strategy improved both the glucose yield and concentration, but only insignificantly. This is because the batch procedure allows to dissolve most of the material at low solids loadings, eliminating the need of a fed-batch strategy.

Increasing the concentration of sulfuric acid in the final step to 7.5% compared to 5% implied that less water was used to dilute the mixture before the hydrolysis step. As a result, the concentration of dissolved cellulose was higher in the hydrolysis step compared to experiments with similar solids loadings in the dissolution step and lower concentrations of sulfuric acid during the hydrolysis. At a solids loading of approximately 0.5 g dry textiles/g acid, there was almost no difference in glucose yield when changing the concentration of sulfuric acid in the hydrolysis. As a result, the final glucose concentration was increased significantly, from 30 g/L to 47 g/L, due to less water present. However, at a higher solids loadings of approximately 0.7 g dry textiles/g acid, the glucose yield decreased significantly, even though the final glucose concentration was still higher, 51 g/L as opposed to 42 g/L, due to the smaller dilution of the system. This means that, at high solids loadings, increasing the acid concentration in the second step allows to produce more concentrated solutions, even though the increase in acid concentration hinders the hydrolysis process.

The degradation of glucose remained on a similar level when increasing the concentration of acid in the hydrolysis for both solids loadings. Thus, the decrease in yield at high solids loadings cannot be attributed to a higher glucose degradation. Further investigation would therefore be required to elucidate the cause of this phenomenon.

4. Conclusions

The glucose yield was low for all experiments when attempting a one-step hydrolysis. The reason for this is that the sulfuric acid showed different effects on the raw material depending on its concentration, effects that when combined lead to a efficient hydrolysis but not when employed separately. Concentrated sulfuric acid exhibited potent dissolving properties, but it was less efficient at hydrolyzing the material to glucose without a substantial formation of by-products. Diluted sulfuric acid, on the other hand, exhibited low dissolving properties, but potent hydrolysis of dissolved material and insignificant formation of byproducts.

Combining the effects of concentrated and diluted sulfuric acid in a two-step hydrolysis resulted in a significant increase in glucose yield: 92% of the theoretical maximum and a glucose concentration of 3 g/L. The final glucose concentration was increased significantly through increasing the solids loading. At higher solids loading, the glucose concentration was approximately 40 g/L while the glucose yield was 84%. This was achieved without any significant formation of byproducts. The glucose concentration was further increased to 50 g/L through other modifications of the procedure, for example a smaller dilution in the second step, although such modifications decreased the glucose yield to 68%.

Two cases of inhibition of hydrolysis were observed during the experiments: when using 60% sulfuric acid in the first step and when increasing the concentration of sulfuric acid in the second step of the hydrolysis. The first case of inhibition is related to the subsequent hydrolysis step after the raw material has been dissolved in 60% acid, as the degree of hydrolysis of dissolved material is significantly lower than compared to experiments using a different concentration of sulfuric acid in the first step. The second case of inhibition occurs when using 7.5% sulfuric acid in the second step, which leads to a decreased degree of hydrolysis but only at high solids loading (above 0.73 g dry textile/g acid). These phenomena might be related to one another, although it is impossible to reach more conclusions without further experimentation.

To conclude, this study has successfully developed a method to chemically transform waste textiles into glucose, resulting in a concentrated product and a high yield. The process uses waste material and the product can be used to produce biofuels, contributing to solve two environmental issues at once. It is important that the large amounts of sulfuric acid used in this process are recycled, both from an economical and environmental viewpoint, and this will certainly come with an added cost. Still, it may be possible that the process could economically outcompete biofuel production from lignocellulosic materials, as a cheaper raw material is used and no enzymes are needed for its saccharification, which would lead to a significant cost reduction in the process.

5. Future work

5. 1. Further upscaling studies

5.1.1. Alternative methods

In this study, our focus has been mainly on one-step and two-step batch acid hydrolysis of textiles. There are several different methods through which acid hydrolysis can be conducted and more of these should be investigated. This study shows that it is possible to produce glucose from cotton-based waste textiles with a high glucose yield and moderately high glucose concentration in the final product. However, there might be other, more efficient methods, using sulfuric acid, that has not yet been tested and therefore, should be investigated. Among other alternatives, one possible method could be to incorporate steam explosion as a step to achieve textile to glucose conversion.

5.1.2. Studies on a larger scale

The process likely behaves differently at a larger scale and conducting experiments in the laboratory is in many aspects different from doing it industrially. Some limitations in the laboratory might be completely non-existent when developing a pilot set-up but similarly, new complications that were not present in the laboratory might arise. Thus, a pilot study would bring more clarity to how such a process might work in practice, which would be valuable for determining the viability of the process.

5.1.3. Downstream processes

Glucose as a product has several applications. It can be used to produce ethanol, commonly used as a transportation fuel, via fermentation but it can also be converted into many other valuable chemicals, like butanediol. Depending on the application, different requirements are posed on the purity and concentration of the product, and the method should be adapted to meet these requirements accordingly. Even though the amounts of by-products formed in our experiments was minimal, fermentation tests need to be performed to evaluate the overall yields of the process.

5.2. Inhibitory effect

5.2.1. Inhibitory effect when dissolving in 60% sulfuric acid

There is clear evidence of a phenomenon occurring during dissolution of the raw material in 60% sulfuric acid that inhibits further hydrolysis. However, this effect is smaller as the temperature of the dissolution step is increased. One plausible reason for this could be that some sort of intermediate molecule forms at those specific conditions that inhibits further hydrolysis and, as the temperature increases, that molecule starts to decompose. If such a molecule does indeed form, it would be interesting to investigate its nature and formation, possibly through NMR measurements, which could allow to determine the underlying mechanism behind this phenomenon.

5.2.2. Inhibitory effect when hydrolyzing in 7.5% sulfuric acid

There is an inhibition effect when the second step of the process is performed at 7.5% acid concentration, but it only occurs at elevated solids loadings and could possibly be related to the phenomenon occurring at dissolution in 60%. However, it is impossible to provide more information about this effect without conducting further investigation on the mechanisms of such inhibition.

5.3. Techno-economic assessment

The production cost of bio-based fuels is in general strongly influenced by the cost of the feedstock (Balan, 2014, Landälv et al., 2018). Since the raw material for the process in this study is waste material, its price is lower and therefore the process is in a good position to compete efficiently with other biofuel production processes. Furthermore, the process in this study does not utilize enzymes and thus gains another economic advantage over lignocellulose-based processes, since enzymes have a large influence on the total production cost because they usually account for 10-20% of the production cost (Joelsson et al., 2016, Landälv et al., 2018). Additionally, the amount of glucose in the liquid product in this study is comparable to other studies which have investigated hydrolysis of lignocellulosic material (Sun and Cheng, 2002) and thus, the cost of purification of the product would be comparable. Thus, it would be of great interest to conduct a techno-economic study for this process to determine its economic viability.

5.4. Feedstock composition

The raw material for this process has been pure cotton bedlinens, a rather homogeneous feedstock. For the process to be viable, it must be able to operate with a more heterogeneous mixture of raw material. It is very likely that a process similar to the one discussed in this study could utilize the cellulosic part of the material in mixed fiber fabrics to a large extent with added possibilities of recycling the other components. Currently, the prospects for such a process look promising and further studies on its robustness in regard to feedstock composition should be conducted.

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