RESEARCH ARTICLE

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Regeneration of Cellulose from a Switchable Ionic Liquid: Toward More Sustainable Cellulose Fibers

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A CO_2 switchable solvent system is investigated to find an environmentally friendlier way to produce man-made cellulose fibers. Cellulose solutions with concentrations from 2 wt% to 8 wt%, based on derivative and non-derivative dissolution approaches, are investigated. Three different switchable solvent systems are tested. After accessing the stability of the produced cellulose solutions, their regeneration is investigated using different alcoholic coagulation media. In order to find a suitable coagulation medium and stable cellulose solution, a dissolution–regeneration cycle is investigated, while trying to minimize the amount of waste by recovering the employed solvents. The process is optimized and the resulting fibers are characterized by infrared (IR) spectroscopy, optical microscopy, as well as scanning electron microscopy.

1. Introduction

The demand of energy is rising globally; fossil fuel resources are decreasing while environmental pollution is increasing drastically.[1] Generally, the alternative to fossil resources, that is, biomass, can be used in two ways: as feedstock for the production of sustainable materials or energetically in order to replace fossil fuels. Scientists worldwide are investigating efficient ways to convert biomass into valuable materials in order to reduce their environmental footprint and replace, for instance, petrochemically derived polymers.[2,3]

Consumers and industries developed an increased interest for products from renewable and environmentally friendly resources. Cellulose offers appealing properties, such as thermal and chemical resistance, combined with biodegradability and biocompatibility. Being the most abundant biopolymer, that is, being cheap and sustainable, cellulose finds application in a wide range of products. The polymeric structure of the "sugar of the plant cell wall" was elucidated by Staudinger in 1920.[4,5] Today, we know that the repeating β-D-glucose units, being covalently linked between the hydroxyl groups of the C4 and C1 carbon atom, provides the biopolymer with its characteristic chemical stability.[6]

To obtain certain products from cellulose as raw material, it needs to be dissolved or modified in order to make it processable. Because of the insolubility of cellulose in most commonly used organic solvents, specific dissolving systems were established with the aim to overcome this obstacle.[5] Since the nineteenth century, scientists focus on the development of suitable solvent systems for cellulose, with the viscose process as the most widely applied technique on an industrial scale. It started in 1890 with the patent of three scientists introducing a process to solubilize cellulose in carbon disulfide in alkaline media. From the obtained viscose solution, cellulose pulp made from wood was regenerated as fibers and used in the textile industry. In the textile industry, the viscose process is still determining the market with an annual world production of around 2.2 million tons in 2002.[6]

However, the viscose process requires hazardous substances and considerable amounts of waste is produced, which is not ideal in terms of green chemistry. Searching for alternative approaches to solubilize cellulose in a more sustainable way has evolved into an active field of research. Generally, green chemistry has become one of the most commonly used concepts towards a sustainable production of chemicals and the prevention of waste.[3,7]

To provide a suitable framework for green chemistry, twelve principles were postulated by Anastas and Warner in 1998. The principles focus on planning the chemical syntheses and the molecular design carefully in order to reduce adverse consequences to humans and the environment.[8] These twelve principles serve as a guideline that suggest to use nontoxic reagents that are safe to handle and are bioderived, while generally avoiding waste.[9]

As reported in several publications, ionic liquids offer a potentially environmentally friendlier way to successfully dissolve cellulose.[5,10] Owing to their characteristic properties, such as nonflammability, low melting point, and low vapor pressure,

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ILs are often considered as green solvents and provide new possibilities in the field of cellulose chemistry. However, the relatively difficult recovery as well as the multistep syntheses of these solvents, in addition to their high costs, still limit the use of ILs for commercial applications and furthermore reduce their sustainability. Their economic use to dissolve cellulose is still under investigation.[9]

The idea of CO_2 switchable solvent systems, reported in 2005, was considered to be a breakthrough in the field of cellulose dissolving systems.[5,11] The main idea, first published by Jessop, was to create a system, in which a non-ionic liquid solvent was converted into an ionic liquid upon exposure to CO_2, with the possibility to reconvert into a non-ionic liquid upon CO_2 removal. The groups of Xie[5] and Jerome[11] applied this new concept and developed two distinct strategies to dissolve cellulose, later defined as derivative and non-derivative approaches. In the derivative approach, CO_2 directly interacts with the hydroxyl groups of cellulose in the presence of a superbase. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is often used in this approach. The interaction results in a reversibly formed complex consisting of a carbonate anion and a respective cation in a solvent like dimethyl sulfoxide (DMSO). In the non-derivative approach, alcohols are used as an additional hydroxyl group source for the solubilization of cellulose.[12,13] Compared to classic ILs, the two approaches show advantages in their dissolving efficiency, sustainability, and lower costs.[3]

Using CO_2 switchable solvent systems, cellulose can be dissolved at 50–60 °C and 2–8 bar CO_2 pressure within 1–3 h. We recently demonstrated that cellulose can be dissolved at 50 °C within 30 min in the presence of DBU and DMSO using the derivative approach and that carbonate anions are formed by the reaction of CO_2 with the hydroxyl groups of cellulose.[13,14]

Furthermore, scientists focus on the optimization of the reaction conditions. Different superbases were tested in DMSO as a solvent. Jerome *et al.* found that, besides the commonly used DBU, the superbases 1,1,3,3-tetramethylguanidine (TMG) and 1,5-diazabicyclo[4.3.0]non-5-en (DBN) also lead to a dissolution of cellulose under CO_2 atmosphere in a comparable manner.[11] The non-derivative approach, investigated by Xie *et al.*, using ethylene glycol (EG) with DMSO and TMG could also dissolve cellulose successfully.[5]

In this work, we employed the reported optimized derivative and non-derivative approaches to dissolve cellulose and focused on studying the regeneration behavior of cellulose solutions in different coagulation media to produce man-made fibers. We thoroughly investigated and optimized the regeneration conditions as well as a possible recovery and recycling of the used solvents. The obtained fibers were characterized via infrared (IR) spectroscopy, optical microscopy, stress–strain measurements and scanning electron microscopic (SEM) analysis to find the optimized conditions for fiber production.

2. Results and Discussion

2.1. Investigations into a Suitable and Stable Cellulose Solution

Cellulose solutions based on non-derivative and derivative approaches of CO_2 switchable solvent systems were prepared.

Table 1. Observations of the produced derivative cellulose solutions of different concentrations are listed with regard on their visually monitored stability over the time.

Cellulose concentration in wt%	Observations
2	1 h no precipitation
3	1 day no precipitation
4	>7 days no precipitation, only change in color
5	1 day no precipitation
6	1 h no precipitation

According to the conditionspreviously introduced by our group,[3] derivative cellulose solutions containing 2–6 wt% cellulose in dimethyl sulfoxide (DMSO) were considered using 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as the superbase (see Experimental Section). An atmospheric CO_2 atmosphere was used, that is, a simple saturation of the solution using a CO_2 filled balloon, enabling an easy handling of the process without the need of any special equipment. Comparing the solutions with regard to their stability, changes over time were visually monitored in tightly closed glass vials and significant differences were observed (see **Table 1**). For detailed information about the used amounts of cellulose, DMSO, and DBU to obtain each cellulose solution, see Table S1, Supporting Information.

As listed in Table 1, the derivative cellulose solution containing 4 wt% cellulose showed the best stability, that is, more than 7 days without any precipitation (only a color change from slightly yellow to orange was observed during this time). A derivative cellulose solution containing 5 or 3 wt% cellulose showed a stability of 1 day; afterwards cellulose started to precipitate from the slightly yellow and viscous solution. In case of the solutions containing 2 % or 6 wt% of cellulose, a stability of 1 h was visually observed, before a precipitation occurred.

Non-derivative cellulose solutions were prepared according to the procedure reported by Xie *et al.*[15] **Table 2** shows different combinations of solvents and bases used to dissolve cellulose in different concentrations, which are listed with obtained stability observations. See Table S2, Supporting Information, for detailed information about used amounts of solvent, cellulose and bases.

First, methanol in combination with DMSO and DBU was used to dissolve cellulose in a concentration of 8 wt%. Applying these literature reported conditions, cellulose could not be dissolved, but cellulose was rather swollen in the solvent. This

Table 2. Observations of produced non-derivative cellulose solutions in different concentrations are listed with regard to their visually monitored stability over the time.

Used solvent and base	Cellulose concentration in wt%	Observations regarding stability of solution
DMSO, DBU, methanol	8	no dissolution
DMSO, DBU, EG	7	1 day no precipitation
DMSO, TMG, EG	7	15 min no precipitation
DMSO, TMG, EG	6	1 day no precipitation

irreproducibility might be due to the use of a different cellulose source. As shown in Table 2 in a second approach, ethylene glycol (EG) was used in combination with DMSO and DBU to dissolve 7 wt% of cellulose. A slightly yellow and viscous solution was obtained, which was stable for 1 day until a precipitation of cellulose was observed. As the next step, two non-derivative cellulose solutions containing 7 and 6 wt% of cellulose, respectively, were produced using EG and DMSO in combination with 1,1,3,3-tetramethylguanidine (TMG) as the superbase. The slightly yellow and viscose solution containing 7 wt% cellulose was only stable for 15 min, whereas the cellulose solution containing 6 wt% was stable for 1 day until cellulose precipitated. For all non-derivative cellulose solutions, a successful dissolution of cellulose was only possible by using a pressure reactor (≈5 bar) instead of a CO_2 filled balloon. For the derivative approach, the stability of dissolved cellulose seems to depend on an optimized ratio between cellulose, DBU, and DMSO, with 4 wt% of cellulose in DMSO and a ratio of 1:3 cellulose:DBU being the most stable one over time.

2.2. Coagulation Media for Regeneration of Dissolved Cellulose as Fibers

Coagulation media based on different organic solvents were investigated for the regeneration of cellulose solutions in order to produce fibers. Water, ethanol, methanol, 2-propanol, and acetone were tested, by simply injecting the cellulose solution into the vigorously stirred coagulation medium using a syringe. These solvents were considered, as they were sustainable options regarding the environmental impact according to an often applied solvent selection guide.[16] By dipping the tip of the capillary into the coagulation medium, while injecting the cellulose solution, the cellulose directly started to precipitate, forming the desired fibers (see **Figure 1**).

In case of acetone, small colorless pieces of precipitated cellulose were obtained in the shape of rather short fibers. Using water as the coagulation medium, cellulose precipitated as flakes. Using the alcohols methanol, ethanol, or 2-propanol as the coagulation medium, cellulose was regenerated as colorless fibers, coiled around the magnetic stirring bar. Ethanol led to the most stable and homogenous fibers (see Figure 1).

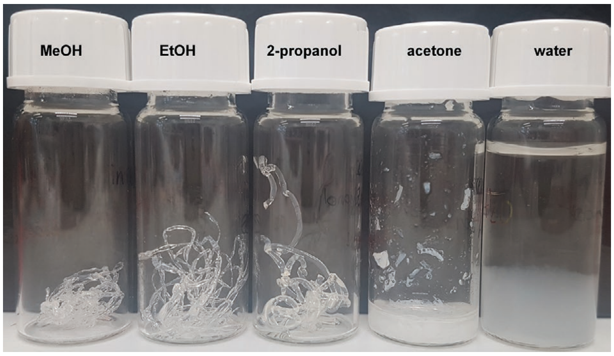

Figure 1. Regenerated cellulose fibers obtained by using 4 wt% derivative cellulose solution injected into different coagulation media (see labeling provided in the figure).

With the found suitable, renewable, and sustainable coagulation medium, cellulose solutions of different concentrations, prepared via derivative and non-derivative approaches, were compared to each other by regarding their ability to form even and homogenous fibers. Using cellulose solutions prepared via the non-derivative approach, even cellulose fibers were obtained regardless of the concentration of the initial solution. The results of the optimization regarding derivative cellulose solutions are visualized in **Figure 2** showing microscopic pictures of each obtained cellulose fiber with 400- and 1000-fold magnification.

As shown in Figure 2 derivative cellulose solutions, in concentrations of 4, 5, or 6 wt%, yielded even fibers, whereas concentrations of 2 and 3 wt% led to uneven, coiled fibers. Besides the coagulation behavior and the ability to form even fibers, it is also important to take the production time and the stability of respective cellulose solutions into account. Derivative cellulose solutions are produced within 30 min, simply by saturating the solution with CO_2 using a balloon and exhibit a stability of up to 7 days. Non-derivative cellulose solutions, in contrast, are produced in 1 h in a pressure reactor and are stable for 1 day. Taking the production of a cellulose solution as well as their coagulation behavior into account, the 4 wt% derivative cellulose solution seemed to be the most suitable one to produce man-made cellulose fibers and was thus further investigated.

2.3. Recovery of Solvents Used for the Regeneration of Cellulose

For the recycling of the used solvents, we focused on removing the coagulation medium ethanol from the remaining mixture of DMSO and DBU. In a recent publication of our group, the successful separation and recovery of DMSO and DBU was demonstrated.[11] In the herein presented study, as a follow-up, the recovered DMSO/DBU mixture was tested for direct reuse for dissolving fresh cellulose. Six recovery tests were performed in total. A rotary evaporator was used at different temperatures and pressures to evaluate the removal of ethanol from the remaining mixture. In **Figure 3** two infrared (IR) spectra showing different results between the use of a rotary evaporator at 40 °C and a vacuum distillation, are exemplarily depicted, clearly showing the ethanol, if not removed completely, with its broad signal at a wavelength of 3600 to 3200 cm^{-1}.

By simply using a rotary evaporator at 40 °C at 10 mbar, it was not possible to completely remove the ethanol from the mixture. However, around 80 % of the used ethanol could be recovered (see Figure 3). In other recovery tests, molecular sieve as well as toluene were tested to remove ethanol or leftovers of water, but were not successful. Finally, also a vacuum distillation (at 90 °C and 20 mbar for 30 min) was tested and resulted in the complete separation of ethanol from the DMSO/DBU mixture, as analyzed by IR spectroscopy (see Figure 3). Importantly, the thus remaining ethanol free DMSO/DBU mixture, in contrast to mixtures still containing ethanol, could be reused directly for dissolving fresh cellulose via the derivative approach without addition of any new solvents or bases. Furthermore, the recovered ethanol could be reused for the regeneration of cellulose.

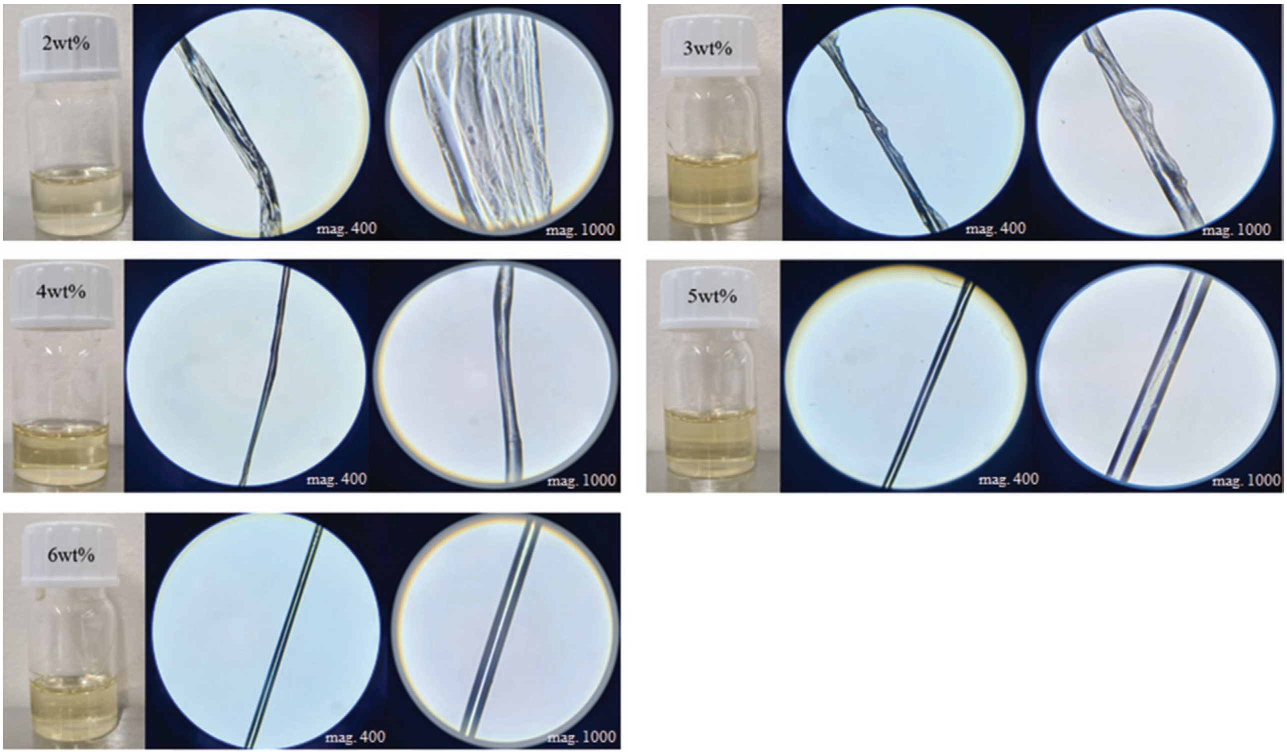

Figure 2. Derivative cellulose solutions of different concentrations displayed with microscopic pictures of the thereof obtained cellulose fibers in 400- and 1000-fold magnification.

To further improve the sustainability of the investigated regeneration process using CO_2 switchable solvent systems, we decided to focus on the elimination of waste. Thus, a so-called dissolution–regeneration cycle is proposed in this study. In each cycle, first 4 wt% cellulose was dissolved in a derivative approach. Then, cellulose was regenerated by precipitation in the coagulation medium in the form of fibers. The fibers were removed from the solution and subsequently, ethanol was removed from the remaining mixture by vacuum distillation. The remaining DMSO/DBU mixture was gravimetrically quantified and reused for another cycle, by adding a calculated amount of cellulose, which was then dissolved. The recovered ethanol was reused for the precipitation of cellulose. It was not necessary to add additional solvent or base during the successive cycles. For a derivative cellulose solution containing 4 wt%, the established dissolution–regeneration cycle could be carried out at least five times. Thus, overall 1.79 g cellulose could be processed using 17.5 g of a DMSO/DBU mixture (recovered and not further analyzed) and 440 mL ethanol.

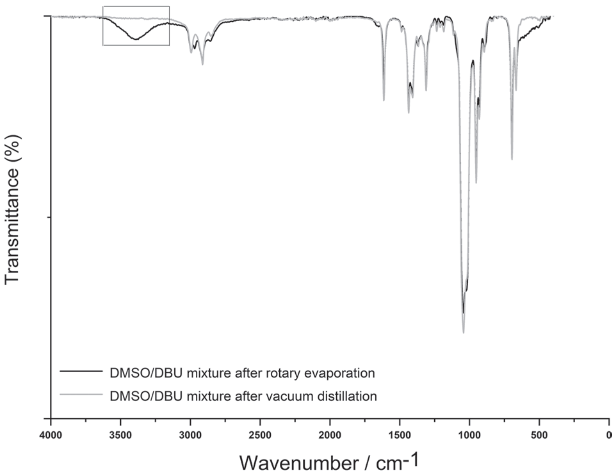

Figure 3. IR spectra of a DMSO/DBU mixture after performing a recovery test by vacuum distillation at 90 °C and 20 mbar, compared to a recovery test using a rotary evaporator at 40 °C and below 10 mbar.

By reusing the DMSO/DBU mixture to dissolve cellulose, the stability of the obtained cellulose solution decreased from <6 h in cycle 2 to <1 h in cycle 5, probably due to the accumulation of water (from cellulose) throughout the cycles. With each additional cycle, the DMSO/DBU mixture furthermore changed its color from colorless in cycle 1 to brownish starting in cycle 4. The viscosity of the cellulose solution increased in each cycle. However, all regenerated fibers remained colorless, but showed differences in their stability. Not 100 % of the used amount of DMSO and DBU could be recovered. During each cycle, 22 %–58 % of DMSO/DBU mixture was lost. The missing amount seemed to be trapped within the cellulose fibers, as typical DBU and DMSO signals are visible in the IR spectra of measured wet, air-dried and oven-dried fibers (1600, 1700, and 900 cm^{-1}, respectively, see **Figure 4**). The recovered DMSO/DBU mixtures could be reused in further regeneration processes, yet the results clearly show that the washing/purification of the fibers needs to be further improved.

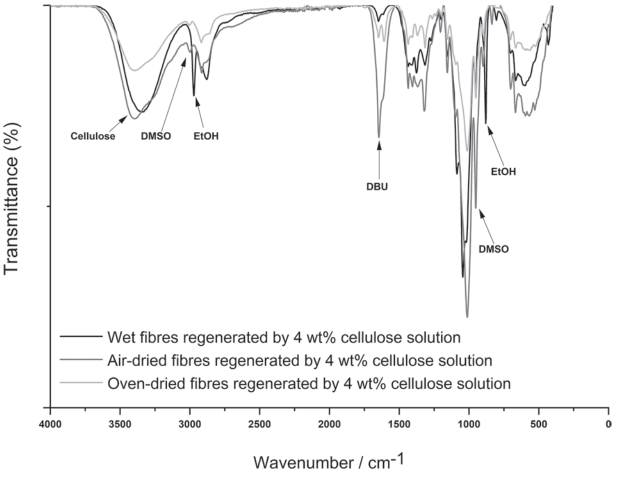

Figure 4. IR spectrum of regenerated cellulose fibers after cycle 1, obtained by using a 4 wt% derivative cellulose solution measured directly from ethanol, measured air-dried, and measured after drying in a vacuum oven at 50 °C.

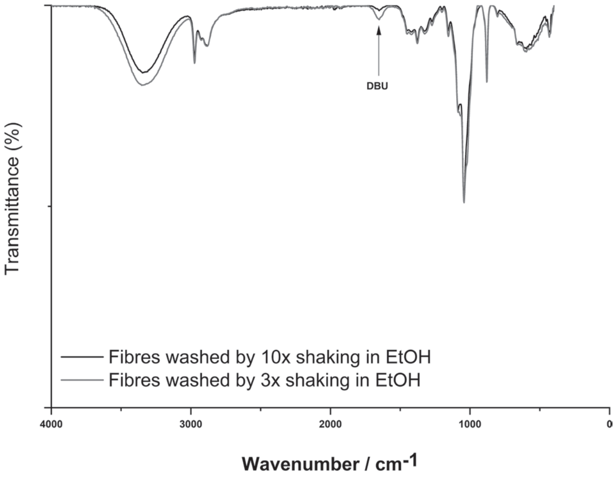

Figure 5. IR spectra of regenerated fibers using a 4 wt% derivative cellulose solution in ethanol; IR measurement performed after washing the fibers three times by shaking in ethanol or ten times shaking.

2.4. Increasing Purity of Cellulose Fibers by Washing Steps

Regarding the properties of the final fibers, not only the production itself is important, but also the subsequent washing steps of the fibers are essential. Leftovers of solvents must be removed before the fibers are dried and used in subsequent applications. Regenerated cellulose fibers, produced by using derivative cellulose solutions and subsequent precipitation in ethanol, might contain DMSO and DBU within their hydrogen bond network. Thus, washing tests were performed with regenerated cellulose fibers to increase their purity. The fibers were analyzed by IR spectroscopy before and after washing. First, the fibers were kept in ethanol for 30 min, for 1–2 h, respectively. However, the fibers' purity did not increase. Using acetone to wash the fibers, for a duration of 2 h, did not show any advantages. Shaking the fibers three times for 60 s in freshly added ethanol, led to a decreased DMSO and DBU signal in the IR spectrum. In the last washing experiment, the fibers where shaken ten times in fresh ethanol for 60 s, leading to complete disappearance of the DMSO signal at a wavelength of 900 cm^{-1} and a significantly decreased DBU signal at 1700 cm^{-1} in the IR spectrum. **Figure 5** shows the IR spectra of regenerated fibers after performing the last two washing tests. Furthermore, washing of fibers in hot solvents like ethanol or methanol did not show any advantages. Extensive washing is thus necessary to produce pure fibers.

Measuring washed and further dried fibers by elementary analysis showed ≈2.10–2.68 wt% DBU and water as impurity. To further remove the remaining DBU from the fibers' hydrogen bond network, a Soxhlet extraction with methanol or ethanol was performed for 6–11 h, decreasing the amount of DBU. Still, elementary analysis revealed an impurity of DBU of ≈1.27–1.75 wt%, after performing a Soxhlet extraction with methanol, also visible in the IR spectrum with a typical DBU signal at 1700 cm^{-1} (see Figure S1, Supporting Information). Thus, the purification was significantly improved, but in the future other approaches, for instance tailored bases with easier removability, have to be considered.

2.5. Characterization of Regenerated Cellulose Fibers

2.5.1. Stress–Strain Measurements

To obtain further information about the fibers' properties, preliminary stress–strain measurements were performed with a regenerated fiber, produced by using a derivative cellulose solution (4 wt%) in ethanol as coagulation medium. Unwashed fibers with a diameter of 90–170 µm showed an elongation value from 0.36–2.54 mm. In comparison, the elongation value for washed fibers (ten times shaking in EtOH) with a diameter of 60–100 µm were in the range of 0.72–2.17 mm. For the breaking strength, unwashed fibers varied from 0.08 to 0.36 N, whereas washed fibers varied from 0.21 to 0.30 N. Compared to viscose fibers produced in the fibers industry, our fibers show a lower elasticity and a larger diameter. According to the stability of fibers, more accurate measurements would be necessary to further compare the results to the characteristics of the viscose fibers obtained in the industry, but these preliminary results clearly show that fibers with useful properties were obtained. For detailed information on the obtained mechanical results, see Table S3, Supporting Information.

2.5.2. Scanning Electron Microscopic Measurements

To further analyze the surface structure of unwashed and washed fibers (ten times shaking in EtOH), scanning electron microscopic (SEM) measurements were carried out. The fibers were compared to each other regarding their surface smoothness using different magnifications ranging from 500× up to 2000× (see **Figure 6**).

Applying a 500× magnification (Figure 6c) on unwashed fibers, the surface shows breaking points and the fibers exhibit a rough surface, also visible in the 1000× magnification picture (Figure 6d). The rough surface is furthermore visible in Figure 6a,b. For washed fibers, a smooth and even surface was observed by SEM with 500× (**Figure 7**a) and 1000× (Figure 7b) magnification.

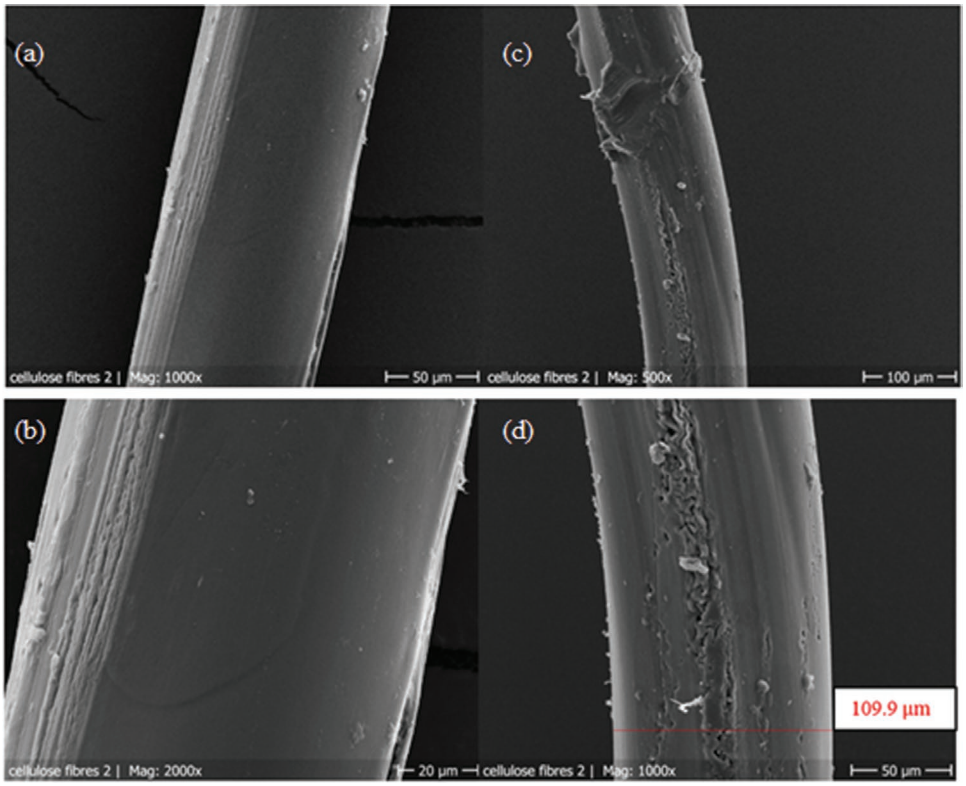

Figure 6. SEM pictures of regenerated unwashed fibers, using different magnifications: a) 1000×, b) 2000×, c) 500×, and d) 1000×.

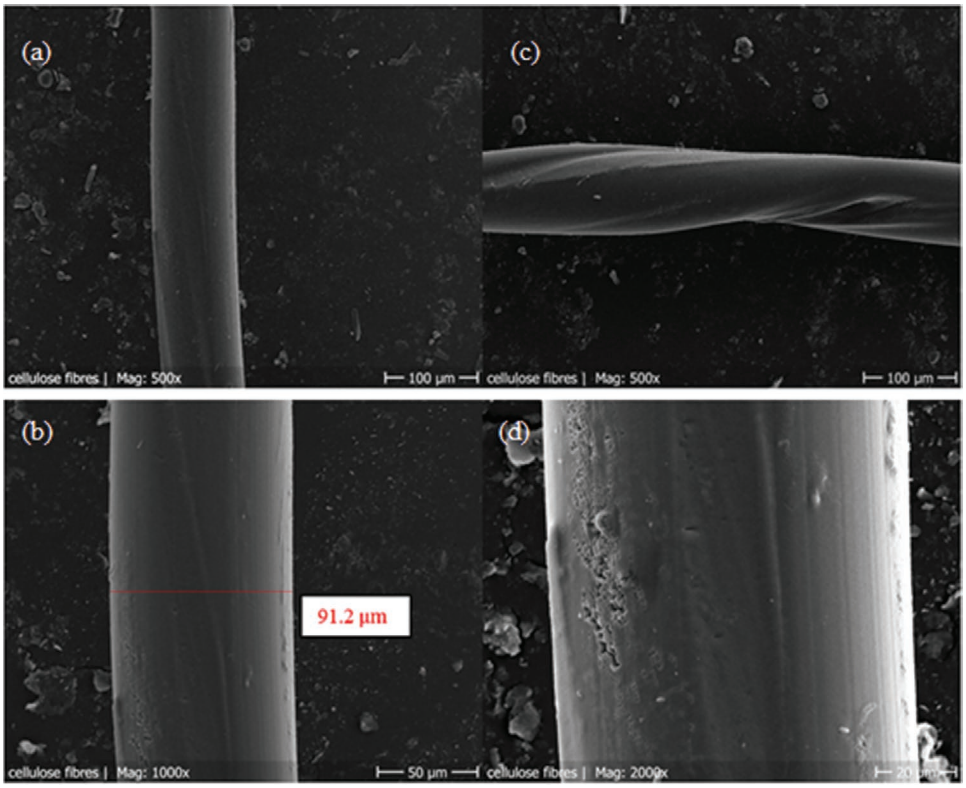

Figure 7. SEM pictures of regenerated washed fibers using different magnifications: a) 500×, b) 1000×, c) 500×, and (d) 2000×.

The washed fibers sometimes showed a twisted structure (Figure 7c), probably caused by the magnetic stirring bar during the regeneration process. Figure 7d also shows that washed fibers may contain some uneven parts on its surface probably caused by leftovers of DBU in the fibers' structure as impurity. However, SEM analysis revealed that washed fibers (ten times shaking in ethanol) show more even and smooth surfaces compared to unwashed fibers and are comparable to viscose fibers of the industry regarding the low surface roughness.

3. Conclusion

Cellulose solutions based on derivative and non-derivative approaches of CO_2 switchable solvent systems were produced and compared to each other according to their stability. For the regeneration of cellulose in the form of fibers, different coagulation media were tested. As the next step, a strategy that allowed for solvent recovery was established. To increase the purity of obtained fibers, different washing steps were tested. Stress–strain measurements were performed for further characterization of the fibers' properties and SEM analysis was performed for information about the surface structure.

A 4 wt% cellulose solution based on a derivative approach of CO_2 switchable solvent systems was found to be the most stable solution with exhibiting a stability of up to 7 days. Ethanol was found to be the most suitable coagulation medium which led to the formation of even fibers, by injecting a cellulose solution. To reuse the DMSO/DBU mixture for the dissolution of cellulose, ethanol must be removed efficiently, which was achieved by vacuum distillation. Finally, a dissolution–regeneration cycle was investigated allowing to reuse regenerated DMSO and DBU for the dissolving of cellulose, which helped to increase the sustainability of the process. Furthermore, the recovered ethanol could be recycled. The cycle of dissolution and regeneration was carried out five times while recovering the used components. These are important steps towards more sustainable cellulose fiber production, but it also has to be clearly mentioned that some challenges, that is, a better recovery of DMS and DBU, remain.

Regarding the washing tests, shaking the fibers ten times in ethanol led to the highest purity of fibers with ≈2.10–2.68 wt% DBU and water impurity. In another experiment, a Soxhlet extraction with methanol was performed for 11 h, but still ≈1.27–1.75 wt% DBU and water remained in the fibers' hydrogen bond network. Performing stress–strain measurements for further characterization of the fibers' properties, unwashed and washed fibers were compared, giving a first indication that fibers with useful mechanical properties can be obtained via this approach. For further structural analysis, SEM was a suitable way to investigate the surface and smoothness of fibers in different magnification, revealing that washing leads to smoother fiber surfaces.

In summary, the experiments demonstrate that the herein presented strategy allows to regenerate cellulose fibers that exhibit attractive properties for further applications in an environmentally friendlier way compared to the widely used viscose process.

4. Experimental Section

Equipment and Chemicals: Syringes and capillaries were used from Bruker (20 mL syringe and capillary of 0.8 × 120 mm). All chemicals were used without further purification. Microcrystalline cellulose (powder) was purchased from Aldrich Chemicals. Acetone (for HPLC, 99.5%) was purchased from Bernd Kraft GmbH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, >98.0%) from Tokyo Chemical Industry, and dimethyl sulfoxide (DMSO, extra dry, 99.7%) from Acros Organics. Ethanol (≥99.8% HPLC grade) was purchased from Fisher Chemicals, ethylene glycol (EG, ≥99.5%) from Riedel-de Häen, 2-propanol (99.9% HPLC grade) from Fisher Scientific, methanol (HPLC grade) from VWR Chemicals, 1,1,3,3-tetramethyl guanidine (TMG, 99%) from Abcr GmbH and toluene (extra dry, 99.85%) from Acriseal.

IR spectroscopy was performed using a Bruker Alpha FT-IR, spectral range: 8000–10 cm^{-1}, evaluated by the computer software OPUS.

All solvent recovery tests were carried out using a rotary evaporator from Heildolph, with >285 °C firepoint oil, auto accurate-sensor, 24 V DC 2 W and Rotavac valve control.

Diameter measurements of regenerated fibers were carried out using a digital caliper of ABSOLUTE AOS, digimatic, Mitutoya Corp. 150 mm, ±0.0001 inch, Model No.: CD-15APX.

For stress–strain measurements, dynamic mechanical analysis instrument was used, from GABO, EPLEXOR 150N, Qualimeter Testanlagen GmbH, Force Transducer Amplifier, 25 N, 40–45 mm, with a deformation of 150%.

A HITACHI S570 scanning electron microscope was used with sample preparation by a sputter coater of Blazers UNION SCD 040.

General Procedure for the Preparation of a Derivative Cellulose Solution Based on CO_2 Switchable Solvent System: Cellulose (microcrystalline; 0.125 g, 0.0770 mmol up to 0.375 g, 0.231 mmol) was suspended in 6.25 mL (7.99 mmol) DMSO. DBU (0.357 g, 0.235 mmol up to 1.07 g, 0.703 mmol) was added to the mixture, stirred at 50 °C, for 30 min, in the presence of CO_2 (1 bar).[3]

The obtained derivative cellulose solutions contained between 2and 6 wt% cellulose. For exact amounts of cellulose, DMSO and DBU used for each cellulose solution produced for this report, see Table S1, Supporting Information.

General Procedure for the Preparation of a Non-Derivative Cellulose Solution Based on CO_2 Switchable Solvent System: Cellulose (microcrystalline, 0.820 g, 0.506 mmol up to 1.15 g, 0.710 mmol) was suspended in 12.7 g (16.3 mmol) DMSO. A strong organic base, that is, DBU (4.20 g, 2.76 mmol) or TMG (4.20 g, 3.65 mmol) and an alcohol, that is, EG[5] (0.984 g, 1.59 mmol up to 1.20 g; 1.93 mmol) or methanol[15] (1.33 g, 4.15 mmol), were added to the mixture. The mixture was stirred for 1 h (EG) or 3 h (methanol) using a pressure reactor at 60 °C, under a CO_2 pressure of ≈6 bar. Afterwards, the mixture was cooled to room temperature under CO_2 atmosphere. For detailed information about the used amounts of the respective components, see Table S2, Supporting Information.

Regeneration of Cellulose in Coagulation Media: A glass vial was filled with 8.00 mL of coagulation medium (methanol, ethanol, water, acetone, or 2-pronanol) and stirred at room temperature. Subsequently, 0.400 mL of a cellulose solution was added into the stirring coagulation medium, by using a syringe with capillary. During the addition, the syringe tip was immersed into the solvent. The cellulose solution was injected slowly, at constant rate.

Solvent Recovery Tests: A derivative cellulose solution containing 4 wt% cellulose in DMSO, prepared with DBU, was regenerated in ethanol. The fibers were removed from the remaining solution, which was used for the following tests. The recovery of ethanol was tested by using a rotary evaporator at different temperature reaching from 40 °C to 80 °C and different pressure settings (90 mbar to <10 mbar). In addition, vacuum distillation was tested for the recovery of ethanol. To further increase the purity of the DMSO/DBU mixture, tests using molecular sieves and toluene were reported.

Dissolution–Regeneration Cycle of Derivative Cellulose Solutions: Each dissolution–regeneration cycle started with the preparation of a derivative cellulose solution. A round-bottom flask was filled with a suitable coagulation medium (ethanol in this case). The regeneration of the cellulose solution was carried out as described above. After the regeneration, the obtained cellulose fibers were washed with ethanol and then separated from the remaining solution. The remaining solution, theoretically consisting of ethanol, DMSO, and DBU, was distilled starting with a rotary evaporator at 40 °C and 90 mbar. Ethanol was then completely removed from the remaining solution by vacuum distillation at 90 °C and 20 mbar. The recovered DMSO/DBU mixture was used to prepare a new cellulose solution by adding the respective amounts of cellulose, thus starting the second cycle.

Washing Tests of Regenerated Cellulose Fibers: The regeneration of the cellulose solution was carried out using 150 mL ethanol and 5 mL cellulose solution. With the regenerated cellulose fibers of six regeneration approaches, six different washing tests were performed. Ethanol was used to further wash the fibres. The fibers were kept 30 min to 2 h in the solvent or the fibers were shake in ethanol three to ten times for 60 s. Furthermore, washing tests were performed identically with the solvent acetone or methanol. Also, washing of fibers in hot solvents was evaluated.

Soxhlet Extraction of Regenerated Cellulose Fibers: The regenerated fibers were washed ten times with ethanol. IR spectroscopy was used for characterization. After washing, the fibers were put into a Soxhlet extractor (3 mL size). For the extraction, 150 mL methanol or ethanol was used. In the first experiment, the solvent was heated to ≈90 °C for 2 h. In further experiments, the extraction was performed for 6–11 h. After he Soxhlet extraction the, fibers were removed and analyzed by IR spectroscopy. The remaining solvent mixture was also measured by IR spectroscopy. Then, the solvent was removed under reduced pressure (40 °C and <300 mbar) and the remaining mixture as well as fibers were analyzed by IR spectroscopy. The IR spectrum of measured regenerated fibers after performing a Soxhlet extraction with methanol for 11 h is depicted in Figure S1, Supporting Information.

Stress–Strain Measurements of Regenerated Cellulose Fibers: The diameter of the obtained fibers was measured with a digital caliper. Regenerated fibers out of a 4 wt% cellulose solution were cut with a scissor into ≈5 cm pieces and were air-dried. For measurements by DMA, the cut fiber piece was clamped between the grips of the DMA instrument. The instrument was set with a grips distance of 15.0 mm and a starting strength of 0.100 Newton. With a rate of 0.500 mm min^{-1}, the instrument measured the maximum elongation in millimeters and its breaking strength in Newton. The instrument was not used in dynamic mode. Thus, stress–strain measurements were performed. For each measured fiber according to measurements 1–7, the regeneration and the washing procedure was always the same. All results are depicted in Table S3, Supporting Information, in detail.

Fiber Structural Analysis by Scanning Electron Microscope (SEM): Fibers regenerated by the use of a 4 wt% cellulose solution were cut with a scissor into ≈1 cm pieces, mounted on a metal stub using a sticky carbon disk. Using a sputter coater, the fibers surface was coated with the conductive material, gold. 30 mA for 30 s were applied leading to coating of 5–10 nm thickness. Then, the coated fiber pieces were measured by SEM. Pictures at 500× to 2000× magnification were taken.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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