The Reactions of Cellulose and Hemicellulose Degradation Products in the Viscose Fibre Spin Bath

Abstract

In viscose fibre production degradation reactions of cellulose and hemicelluloses do occur. Degradation products from the alkaline degradation steps, i.e. steeping and pre-ageing, are apparently diverted into the acidic spin bath, where they undergo further reactions. Although the primary degradation products are well characterised, further reactions of these degradation products are hardly investigated. We tested the reactivity of degradation products under conditions, which prevail in the acidic spinning media of the viscose process. The studied chemical species were xylose, glucose, isosaccharinic acid, lactic acid and glycolic acid. We found strong indications that intermediate products, such as furfural and derivatives thereof, are formed, which readily polymerize and yield solid deposits. We showed that xylose, glucose and isosaccharinic acid trigger the subsequent formation of precipitants. Among the model compounds studied, xylose formed solid deposits most rapidly. The promoting effect of hydrogen sulfide on the formation of deposits was verified as well. Suspended solid particles act as crystallization points.

Keywords: Viscose, deposits, cellulose degradation, glucose, xylose, isosaccharinic acid, lactic acid, glycolic acid, furfural

Introduction

In viscose fibre production cellulose is subject to a sequence of chemical conversion processes. Initially the cellulose is steeped with sodium hydroxide lye, which activates cellulose and affords the so-called alkali cellulose. The alkali cellulose is pre-aged with the aim to adjust the molar mass of the cellulose. The aged alkali cellulose is then xanthogenated by reaction with carbon disulfide. The xanthogenate groups facilitate the dissolution of the cellulose in caustic lye. A viscous mass is obtained, the so called viscose dope. This dope is spun into the acidic spin bath. The xanthogenate groups are decomposed, carbon disulfide is released and the cellulose precipitated in the form of viscose fibres. Then the fibre is thoroughly washed, cut, after-treated and dried.

These harsh chemical conditions cellulose is exposed to cause some degradation of the polysaccharidic material. The degradation reactions which occur under alkaline conditions are well known. Degradation reactions in acidic media are reported in literature as well. However, the chemical behaviour of the degradation products in the viscose process have hardly been an issue up to now although the degradation products accumulate in the closed and recycled process streams having an important impact on the viscose fibre product quality. Degradation reactions occur mostly during alkaline steeping and the subsequent pre-ageing of the alkali cellulose. In principle three different cellulose degradation mechanisms can be discerned under alkaline conditions:
- End-wise degradation (peeling)
- Alkaline chain scission
- Aerobic (oxidative) alkaline degradation

These mechanisms can be differentiated by the conditions, under which they occur, and the resulting degradation products. The end-wise degradation (peeling) (Figure 1) does not involve air (oxygen) and typically occurs at moderate temperatures. In the peeling reaction, the anhydroglucose unit is split off (peeled off) one by one starting from the reducing sugar end. Initially in the open-ring structure the carbonyl group moves from position 1 to position 2 of the glucose unit in an Alberda-van-Eckstein-Lobry-de-Bruijn transformation (EBT)\textsuperscript{11}. After deprotonation of the enol hydroxyl group an alkoxy-group can be easily eliminated from the beta-position of the enolate. The polysaccharide chain is eliminated from the C4-atom by this beta-alkoxy elimination (see Figure 1). A vicinal dicarboxyl compound, 4-deoxy-D-glycero-2,3-hexodiulose\textsuperscript{9, 10} is yielded.

Under alkaline conditions the obtained dicarboxyl compound undergoes further reactions. Most important is a benzylic acid rearrangement yielding iso- and meta-saccharinic acid\textsuperscript{9, 10}. The meta-saccharinic acid is obtained via a benzylic acid rearrangement of 4-deoxy-D-glycero-1,2-hexodiulose, which is formed from 4-deoxy-D-glycero-2,3-hexodiulose by an EBT. The formation of glucoisosaccharinic acid is depicted in Figure 2. A retro-aldol reaction yields products of lower mass (Figure 3)\textsuperscript{9, 12}. A number of degradation products was found, and not all formation mechanisms of them are clear. Beside meta- and iso-saccharinic acids, lactic acid and 2,3-dihydroxypropanoic acid are typical degradation products\textsuperscript{9}.

The alkaline scission occurs only at elevated temperatures, above 170°C\textsuperscript{9, 10}. It is a hydrolytic scission of glycosidic bonds, catalysed by high hydroxyl ion concentrations. It requires conformational changes from the 4C\textsubscript{1} into the 1C\textsubscript{4} chair conformation, which is only possible at higher temperatures\textsuperscript{10}. In principle every glycosidic bond in the polysaccharide chain can be cleaved this way. As a consequence, fragments of larger molecular mass are formed, from oligomeric to polymeric size.

The aerobic (oxidative) alkaline degradation mechanism takes place in the presence of air and oxygen. By oxidation, a carbonyl group is formed on an anhydroglucose-unit, which in turn immediately leads to chain scission under alkaline conditions. This happens again by beta-alkoxy elimination (compare Figure 1), which in contrast to the endwise peeling might occur anywhere along the chain, wherever an oxidized groups has been introduced before. As a result fragments of oligomeric to polymeric character are formed.

The degradation mechanisms described are not only affecting cellulose but also hemicellulose, for instance xylan from hardwood.

The acidic degradation of cellulose proceeds accor-
ding to a typical hydrolytic reaction mechanism. At first the oxygen atom of the glycosidic bond is protonated. The bond to the adjacent C1 atom breaks, forming a carbenium ion which is attacked by a water molecule in the next step. After the release of a proton a neutral glucose unit and a neutral residual cellulose chain is formed. Monomeric glucose units are predominantly formed. Oligomeric fragments scarcely emerge due to the kinetics of bond scission. However, it is not clear, which role acidic degradation plays in the viscose process, as the cellulose and the fibre, respectively, remain only a few seconds in the acidic spin bath during the spinning step. The extent of degradation depends, besides the chemical matrix (pH, oxygen access) and the temperature also on the supermolecular structure of cellulose. The accessibility of the cellulose chains with regard to degrading agents, for instance the OH- anion, is essential. Thus the packing and crystallinity of cellulose plays a key role for the extent of degradation. The more accessible the cellulose packing is for the degrading reagent, the faster the degradation is.

The alkaline degradation mechanisms play a role – as mentioned – predominantly during the steeping of pulp, the aging of alkali cellulose and within the corresponding lyes. The steeped pulp is pressed to yield the alkali cellulose. The lye, separated from the pulp slurry, is recycled. One part is used for repeated steeping, another part of this lye is used for the dissolution of the xanthogenated cellulose, which yields the viscose dope. Since the viscose dope is spun into the spinning bath, the alkaline degradation products end up in the acidic spinning bath. This change of the chemical properties of the matrix is able to induce chemical reactions and conversions of the degradation products.

It is well known that sugars dehydrate to furan derivatives under acidic conditions at higher temperatures. Xylose reacts to furfural whereas glucose is converted to hydroxymethylfurfural. Both reactions might occur in the acidic spin bath of the viscose process. The monomeric sugars can be formed from acidic degradation reactions of hemicellulose and cellulose fragments, which are soluble in the acidic spin bath. Polysaccharides, which are not soluble, cannot act as source. They reside in the spin bath only for a few seconds during the spinning step. However, fragments from polymeric polysaccharides, which are formed for instance by alkaline oxidations during ageing, might be of such low molecular mass that they dissolve in the acidic spinning bath. Due to recycling of the spin bath longer residence times result, upon which those soluble oligomers are likely to be hydrolysed to monomers. It is well-established that furfural and its derivatives readily polymerize to insoluble molecular species, which precipitate and form deposits. The occurrence of deposits in the spin bath circuits of industrial facilities can be observed indeed. These deposits are objectionable for production since in the staple fibre they are detrimental for product quality. The formation of furfural and its derivatives from cellulose degradation products is one possible reason for the formation of those depo-
sits. It is unknown, which degradation products form deposits. Furthermore it is not clear, if degradation products of cellulose or hemicellulose can form precipitates under the conditions prevailing in the acidic spin bath. In deliberate furfural production, for instance, temperatures above 150°C are used\(^{14, 16}\); temperatures which are never reached in the viscose spin bath. In this paper we present results, which indicate that the formation of furfural and its derivatives plays indeed a key role for the occurrence of deposits. We further limited the bandwidth of degradation products leading to precipitates. As product quality builds the centre of interest, a number of factors i.e. the influence of hydrogen sulfide and suspended solids, were studied with regard to deposit formation in the viscose process.

**Materials and Methods**

In the first step we checked, if and in particular which hemicellulose degradation products form solid contaminations under industrial process conditions. Therefore the conditions in the acidic viscose spin bath have been simulated in the laboratory. A solution, analogous to the spin bath, has been heated for a defined time. 100 mL of a laboratory prepared spin bath, i.e. an aqueous solution containing H\(_2\)SO\(_4\), ZnSO\(_4\) and Na\(_2\)SO\(_4\), was heated to 90°C. The chemical species xylose, glucose, glucoisosaccharinic acid, lactic acid and glycolic acid, which are known to be cellulose or hemicellulose degradation products\(^9\), were added at defined concentrations. If not stated otherwise, 500 mg were dissolved in 100 mL, resulting in a concentration of 5 g/L. Samples were taken for analysis by UV-Vis spectroscopy with an Agilent 5483 instrument. After heating at the elevated temperature of 90°C for 72 h the solid precipitants formed were separated, sucked off via a suction filter, dried and weighted.

### Results and Discussion

During the thermal impact experiments with addition of xylose, glucose and glucoisosaccharinic acid to a simulated spinning bath the colour of the reaction solution turned yellow. In case of lactic acid and glycolic acid no such colouring was observed. We noticed a distinct absorption band around 280 nm. For xylose the absorption band was exactly located at 278 nm and for glucose at 285 nm. In the visible region a broad, undefined absorption over the whole wavelength area evolved. The colouring of the reaction solution as well as the intensity of the band increased with continued heating. Therefore we assigned the band around 280 nm to a primary degradation product. Furfural absorbs at 280 nm as well. This indicates that the first degradation product of xylose, which is formed at a temperature of 90°C, is furfural, which is in accordance with the hypothesis derived from literature\(^{14, 16, 19-21}\). The slight difference of 2 nm between the absorption maximum of the xylose conversion product and the absorption maximum of furfural might be caused by side products. The absorption of the glucose degradation product at 285 nm is probably mainly derived from 4-hydroxymethylfurfural. Figure 6 shows absorption bands of the glucose degradation product, the xylose degradation product and furfural. Furthermore the progress of the formation of xylose, which is formed at a temperature of 90°C, is furfural, which is in accordance with the hypothesis derived from literature\(^{14, 16, 19-21}\). The slight difference of 2 nm between the absorption maximum of the xylose conversion product and the absorption maximum of furfural might be caused by side products. The absorption of the glucose degradation product at 285 nm is probably mainly derived from 4-hydroxymethylfurfural. Figure 6 shows absorption bands of the glucose degradation product, the xylose degradation product and furfural in comparison.

![Figure 6. Comparison of UV-spectra of degradation products of xylose and glucose with the spectrum of furfural.](image)

![Figure 7. Increase of the UV-absorption band at ~280 nm after different times at the elevated temperature of 90°C in synthetic viscose spin bath.](image)
The thermal impact experiments applying xylose, glucose and glucoisosaccharinic acid resulted in the formation of solid dark precipitants. In case of lactic acid and glycolic acid no formation of solids was detected by thermal impact experiments. This is in agreement with the hypothesis, that the solid deposits are formed via furfural and its derivatives. The increase of the UV-band at ~280 nm indicates that xylose degrades faster than glucose. In connection with the hypothesis, that the solids are formed by polymerization reactions from furfural (and its derivatives) it could be hypothesized, that xylose also forms solid deposits faster than glucose. In order to verify this hypothesis we carried out thermal impact experiments with an initial concentration of 20 g/L of xylose, glucose or glucoisosaccharinic acid and a total volume of 100 mL. After heating to 90°C for 72 h we measured 218 mg deposits for xylose, 46 mg for glucose and 16 mg for glucoisosaccharinic acid (Figure 8). This supports our hypothesis that xylose degrades and forms solid deposits faster than glucose and glucoisosaccharinic acid. We assume that the initial isomerization step required for furan formation is faster in the case of xylose as compared to glucose.

Besides the chemical degradation of polysaccharides discussed so far, also hydrogen disulfide present in the spin bath of the industrial process might play an important role. Hydrogen disulfide is released via a side reaction during the de-xanthogenation in the spinning step. Considering furfural formation as formulated in Figure 4 and the nucleophilic character of the sulfide ion the question arises, if the sulfide ion could participate in the reaction. In order to answer that question we carried out thermal impact experiments with xylose as test species (5 g/L or 33.3 mmol/L, 100 mL batch) with and without the addition of hydrogen sulfide. 0.64 mol of gaseous H$_2$S were discharged into the reaction mixture (of 100 mL) during the first two hours. The experiment without hydrogen disulfide yielded 80 mg solid deposits after 72 hours whereas the experiment with hydrogen disulfide yielded 118 mg. This represents a significant increase by 38 mg and proves that hydrogen disulfide promotes the precipitate formation. The participation of sulfide ions in the reactions of the organic species is only one possibility, the sulfide could affect the formation of solids. Raman spectra of the formed precipitate proved, that elemental sulphur is formed under the test conditions as well.

In a further set of experiments we hypothesized if the presence of solids accelerates the formation of solid precipitants. In order to verify this hypothesis, we performed three separate thermal impact experiments, with xylose as source material, and with the addition of 100 mg of fine particles of silicon dioxide and activated carbon in two separated experiments. In order to determine the mass of the formed precipitates, from the mass of total solids filtered off after the thermal impact experiment the mass of initially added particle material was subtracted. The yield of solid precipitates of 80 mg was increased to 95 mg by silicon dioxide and to 131 mg by activated carbon. Since an increase is obtained with both, very different particle materials, we concluded that particles in the solution somehow act as seed nuclei. The distinctly higher increase by activated carbon probably is owed to its high effective surface area and surface structure. The determined mass of precipitates in the case of addition of activated carbon as well might be increased by material, absorbed by the activated carbon.

### Conclusions

The concept of thermal impact experiments in viscose spin bathes proved to be a valuable tool for the investigation of reactions of dissolved cellulose degradation products under process conditions. The situation in the acidic spin bath of industrial production was simulated. We tested the degradation products xylose, glucose, glucoisosaccharinic acid, lactic acid and glycolic acid for their reactivity in acidic media. UV spectra of initially soluble degradation products of xylose and glucose supported the hypothesis that furfural or a derivative thereof is formed. Extended reaction time of 72 h at 90°C lead to solid precipitates from xylose, glucose and glucoisosaccharinic acid. Upon applying xylose the highest amount of precipitates was formed. Lactic acid and glycolic acid do not undergo any further reaction. This is in accordance with the hypothesis that further reactions proceed via furfural (and its derivatives).
We were also able to prove, that hydrogen sulfide promotes the formation of solid deposits. This is of relevance, as hydrogen sulfide is released by a side reaction during the spinning step of the viscose process. Solids, suspended in an acidic reaction medium, promote the formation of solid contaminants as well.

Acknowledgements

This work was funded by the Austrian research funding association (FFG) under the scope of the COMET programme within the research project “Industrial Methods for Process Analytical Chemistry - From Measurement Technologies to Information Systems (IMPACts)” (contract # 843546). This programme is promoted by BMVIT, BMWFW, the federal state of Upper and Lower Austria. We also thank Kelheim Fibres GmbH and Lenzing AG for their in-kind contributions.

References


