

CRYSTAL STRUCTURE CHANGE OF CELLULOSE DUE TO GASEOUS AMMONIA TREATMENT

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Dissolving pulp was treated with ammonia gas at 20 °C at different pressure levels. The modified pulp was analysed with regard to the change in crystal structure from cellulose I to III. X-ray diffraction and Raman spectroscopy were used as analytical methods. It was found that the transformation of cellulose from cellulose I to III takes place above a defined pressure level, which could be recorded continuously as a function of pressure. Below the characteristic pressure level, the cellulose is still present as cellulose I after treatment. This pressure level is lowered by the presence of water. The ammonia gas is therefore able to swell the crystalline areas of the cellulose starting from a defined process intensity, causing the cellulose to recrystallize in a different structure. Finally, the cellulose III obtained was partially converted back into cellulose I by water boiling.

Keywords: gaseous ammonia, cellulose III, XRD, Raman spectroscopy

INTRODUCTION

On the way to a sustainable economy, the use of wood plays an important role. It is renewable, versatile, can be used in cascades and at the end of its economic life cycle it can again serve as a source for thermal energy. As carbon remains bound over the lifetime of a product, the material use of wood plays an important role. In order to enable the widest possible field of application for wood, it is necessary to adapt the properties of the wood specifically to the requirements of the product. In wood science, this is generally known as wood modification. A special modification method that leads to various changes in the wood is the treatment with ammonia. In addition to changes in many technical parameters of the wood, changes in the cellulose were also observed in the course of the investigations carried out.^{1,2} These changes are in the focus of the research described here.

Ammonia and water have many similar properties. They are both molecules of similar size and both are strong dipoles. They interact with the cellulose by forming hydrogen bonds.

However, unlike water, ammonia and ammonia derivatives are able to swell the crystalline regions of cellulose and cause a change in the crystal structure.³

A simplified overview of the conversion of cellulose is shown in Figure 1. Native cellulose is converted by the ammonia to amorphous ammonia cellulose. After the ammonia is removed, the cellulose recrystallizes into a modified crystal structure, cellulose III.⁶ Depending on whether cellulose I or II is used as the starting material, the product is named cellulose III_I or III_{II}.⁷ As only cellulose I is used as a starting material in this investigation, cellulose III_I will be referred to as cellulose III. There are various options to choose from as a reactant for the conversion. Usually liquid ammonia⁸⁻¹⁰ or amines are used for the conversion.^{4,11} However, the conversion in gaseous ammonia has been little investigated so far. Gaseous ammonia is particularly advantageous for treating wood, which consists of approximately 50% cellulose. The wood is very

easy to impregnate and the treatment intensity can be controlled by varying the gas pressure.

Against this background, the aim of this paper is to investigate the effect of gaseous ammonia on cellulose and to find out whether a transformation of the crystalline structure of cellulose occurs. Further, the gas pressure at which this transformation takes place and the influence of the moisture of the initial material before the treatment are to be investigated. The possibility of reconversion of cellulose III to cellulose I should also be examined.

EXPERIMENTAL

Starting material

Dissolving pulp (Sappi SAI-VSF, sulphite, eucalyptus) was used as the starting material for the tests. A sheet was cut into 2 cm x 2 cm pieces, which were then modified using different methods. Since the influence of the initial moisture content before the gaseous ammonia treatment was also to be investigated, one part of the material was dried in an oven (103 °C) and the other part was stored in an air-conditioned environment at 20 °C and 65% relative humidity.

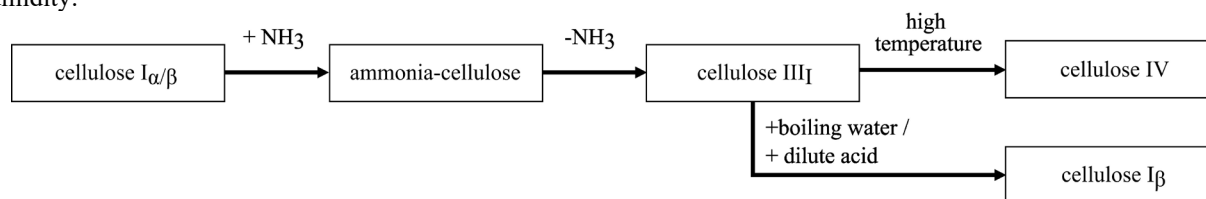


Figure 1: Change of crystal structure due to ammonia treatment and its reconversion (adapted from ^{4,5})

Table 1
Ammonia pressure levels

Ratio p_i/p_s^a	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.7	0.9
Pressure, absolute (kPa)	106	171	257	343	429	514	600	686	771

^{a)} p_i : partial pressure, p_s : saturated steam pressure (at 20 °C: 857 kPa)

Treatments for delimitation

In order to compare the results obtained here with literature data, one specimen (dry prior to treatment) was also treated with liquid ammonia. Following the reaction by Agarwal¹² and Sawada,¹⁰ the cellulose was treated in a round bottom flask with liquid ammonia for 4 hours. However, instead of liquid nitrogen, a mixture of acetone and dry ice was used to cool the round bottom flask.

Furthermore, the results should also be differentiated from cellulose II as part of the investigations. To obtain cellulose II, an additional sample was treated in NaOH (20%) at room temperature for 24 hours in a mercerisation process.¹³

Gaseous ammonia treatment

The gaseous ammonia treatment was carried out in a stainless steel autoclave, whose shell was temperature-controlled to 20 °C. The treatment was carried out for 24 hours and at 9 different pressure levels. The gas pressure was kept constant with an automatically controlled valve with a hysteresis of ± 3 kPa relative to the set target pressure. The pressure levels are listed in Table 1. They are given as a ratio of partial pressure to saturated steam pressure.

Due to the relative measuring sensor of the automatic pressure control, the lowest pressure level was slightly above ambient pressure. The highest pressure level was close to saturated steam pressure to avoid condensation effects.

Gaseous ammonia treatment begins with the positioning of a specimen inside of the autoclave and closing it. The autoclave was then evacuated to a final pressure of 5 kPa for 5 minutes. The ammonia gas was then fed from a gas cylinder (99.98% purity) into the autoclave up to the defined pressure and kept constant. After 24 hours, the ammonia gas was drained and the specimen was removed for ventilated storage in a laboratory fume hood.

Analysis of cellulose I, II and III

The cellulose polymorphs were analysed using two different methods. Basic analyses were carried out using X-ray diffraction. The comprehensive investigation of the different pressure levels was then carried out using Raman spectroscopy.

X-ray diffraction was carried out on a diffractometer from Malvern Analytical/Empyrean, which was configured in the reflection position. The radiation from an X-ray tube (Empyrean Cu LFF HR) was limited to the wavelength $K_{\alpha 1}$ (0.1540598 nm) using a monochromator (Inc. beam Johansson 1xGe111 Cu/Co). Two measurements were taken per specimen and added together. The diffraction angle 2θ was analysed in the range from 10° to 40° with a

resolution of 0.0131° . The sample holder (stainless steel) rotated at 15 rpm. The samples were 10 mm x 10 mm x 2 mm in size and were pressed mechanically into small plates to increase their density. The tests included the cellulose I (reference) and II samples and the liquid ammonia treated sample. One of the gas treated samples was analysed: $p_i/p_s = 0.9$ (highest pressure level) and dry prior to treatment.

The Raman spectrometer used was a Bruker MultiRAM (1064 nm Nd:YAG laser). The measurement parameters were: 300 mW, 200 scans and a resolution of $1/\text{cm}^{-1}$. The cellulose was pressed into appropriate crucibles for the Raman measurements. Analysis was performed using OPUS 7.5 software (Bruker). All Raman spectra were baseline corrected. The band at a wavelength of 1096 cm^{-1} was used as a normalisation, since it remains unchanged for cellulose I, II and III.¹² For this purpose, a min-max normalisation was performed in the range between $900 - 1100 \text{ cm}^{-1}$. Only a corresponding section is shown in the main part of this paper. Both the samples for delimitation and the complete pressure levels and moisture contents were analysed.

Reconversion cellulose III to cellulose I

The studies should also consider whether cellulose III can be converted back into cellulose I and whether this can be measured using the methods used here. In accordance with Roche and Chanzy,¹¹ a gaseous treated sample ($p_i/p_s = 0.9$, dry prior to treatment) was boiled in water for 30 minutes. The sample was measured again with X-ray diffraction and Raman spectroscopy.

RESULTS AND DISCUSSION

The results of the X-ray diffraction are shown in Figure 2 and the strong reflexes have been marked. These were determined with the software Cambridge Crystallographic Data Centre/Mercury 2021 using the additional data from French¹⁴ as input parameters (steps 0.01° , peak shape FWHM: 1.5°). In the case of cellulose I, it can be assumed that both cellulose I_α and I_β are present. As cellulose I_β is more dominant in lignifying

plants, the values of this polymorph have been used here.¹⁵ However, it should be noted that the differences in the diffractogram are only minor and have no significance in comparison with the other polymorphs. As can be seen in the diagram, the measured results for cellulose I are consistent with the literature data presented.

The self-produced cellulose II is also confirmed by the literature data and can be reliably distinguished from the other polymorphs. In the case of cellulose III, the results of the liquid and gaseous treatment are very different from each other. In the case of the gaseous treatment, the main and secondary reflexes are very well developed and agree with the literature data. In the case of the liquid ammonia treatment, only the main reflex at 20.8° is clearly recognisable. This is probably due to thermodynamic reasons, as the conversion temperature is significantly lower compared to the gaseous treatment and the treatment time is shorter. In both cases, however, it can be assumed that cellulose III has been successfully obtained, cellulose II is not existent and cellulose I is no longer present.

The relevant excerpt of the Raman spectroscopy results is shown in Figure 3. The bands identified by Agarwal¹² as medium or strong bands are shown as dashed lines. They are included for comparison with the literature data. The measured spectra show very good agreement with these data. Cellulose I is very different from the other results and can therefore be identified with high reliability using Raman spectroscopy. However, the spectrograms of cellulose II and III are very different from those of cellulose I, but are themselves very similar and, unlike X-ray diffraction, cannot be distinguished with certainty. In detail, cellulose III produced by treatment with liquid ammonia, is very similar to cellulose II in the selected wavenumber range.

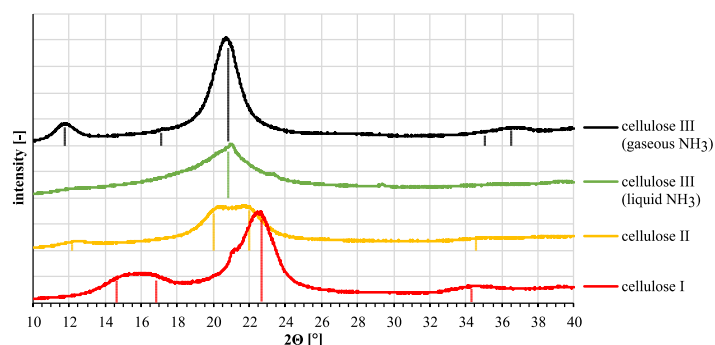


Figure 2: X-ray diffractograms of cellulose polymorphs and main reflexes

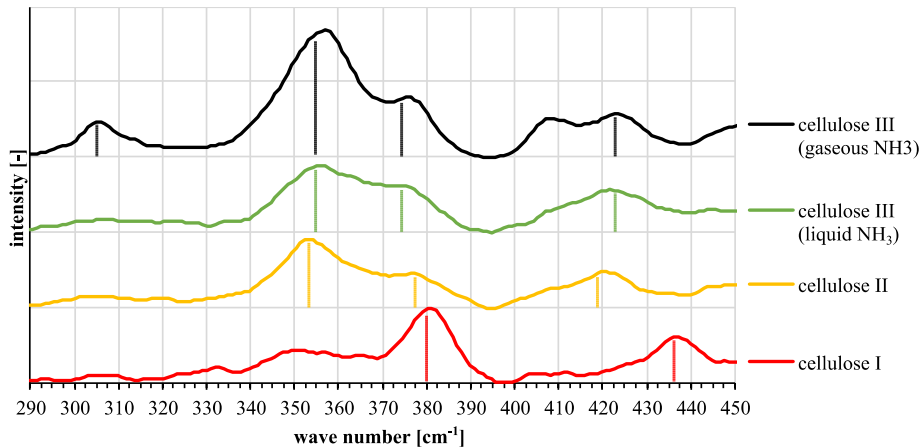


Figure 3: Raman spectrograms of cellulose polymorphs, and medium and strong bands identified by Agarwal¹²

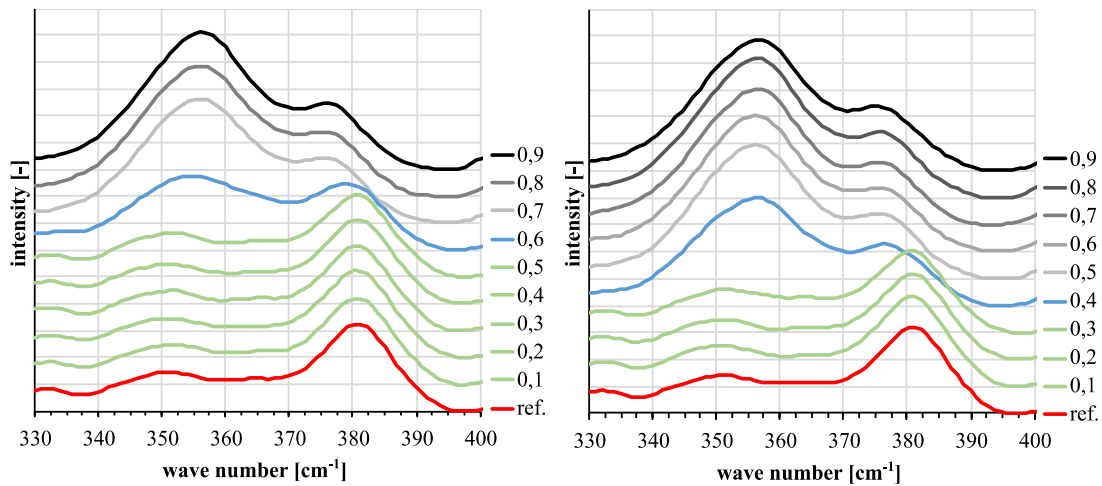


Figure 4: Raman spectrograms of dissolving pulp treated with gaseous ammonia; left: dry prior to treatment (103 °C), right: humid prior to treatment (20 °C, 65% RH; ref.: reference; gas pressure is given in p_i/p_s)

Cellulose III, which was produced with gaseous ammonia, again shows more pronounced bands compared to the liquid treated sample.

For cellulose I, there is a strong band at 380 cm^{-1} in the selected wave number range. Cellulose III, however, shows a strong band at 355 cm^{-1} . In the further evaluation, this shift should be used to identify the conversion from cellulose I to III. The required wavenumber range is therefore reduced to the range with the strong bands from 330 to 400 cm^{-1} . The presence of cellulose II has already been excluded by X-ray diffraction and can be disregarded in the further discussion.

Based on the preliminary investigation, the spectrograms shown in Figure 4 only contain spectrograms of polymorphs cellulose I and III. The untreated cellulose serves as a reference for the measurements and therefore contains only

cellulose I (reference). As the ammonia gas pressure was varied in 9 ascending pressure levels in the experiments, the spectrograms are shown in the figure according to the increasing pressure.

At low pressure levels, no difference can be seen between the reference sample and the treated samples. The spectrogram changes with increasing pressure: the cellulose I band at 380 cm^{-1} decreases and the cellulose III band at 355 cm^{-1} appears. This transformation begins at a pressure level of $p_i/p_s = 0.6$ for samples that were dry before treatment. For previously humid samples, the pressure level of an initial change is lowered to a pressure level of $p_i/p_s = 0.4$. The additional humidity apparently acts like a catalyst. Increasing the gas pressure to the maximum pressure of $p_i/p_s = 0.9$ leads to a more pronounced appearance of the bands and the cellulose was completely converted to polymorph III.

The changes measured and described here relate only to a before-and-after view. If the results are related to the process during the ammonia treatment, the following can be stated: at low treatment pressure, the ammonia only swells the amorphous areas of the cellulose, as for example is also known for swelling caused by water. At higher pressure or treatment intensity respectively, the ammonia begins to swell the crystalline areas of the cellulose and forms amorphous ammonia cellulose. After the treatment, when the ammonia evaporates again, the cellulose recrystallizes in a modified crystal structure, namely cellulose III.

The polymorph cellulose III is metastable and can be converted back into cellulose I. The reversion may open up further possibilities, as it represents an additional phase transformation and could be utilised technologically. The reversion was carried out according to Roche

and Chanzy,¹¹ by boiling in water for 30 minutes. The phase transformation was analysed using X-ray diffraction and Raman spectroscopy, the results of which are shown in Figure 5 and Figure 6.

The reconverted cellulose shows properties of cellulose I and also cellulose III, as can be seen both from the reflexes in Figure 5 and from the bands in Figure 6. It can therefore be assumed that a mixture of two phases is present, but the percentages of these phases were not determined. Although the experiment was carried out according to the literature, complete conversion was not achieved. In a supplementary investigation, the boiling time was therefore increased to 300 minutes, but in the Raman spectrogram this did not differ from the 30-minute boiling time. The reaction time therefore does not appear to be responsible for the incomplete reversion.

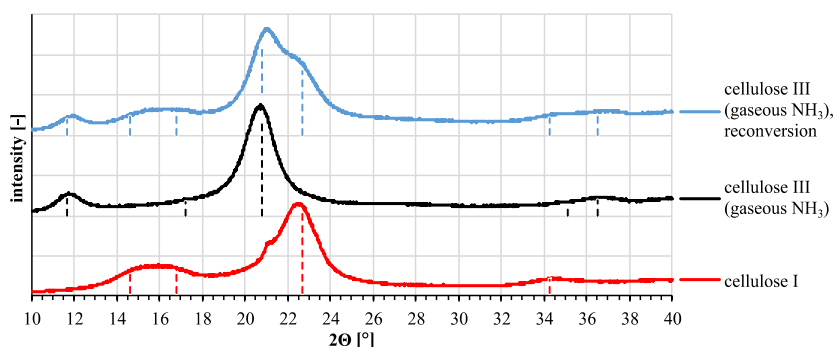


Figure 5: X-ray diffractograms of cellulose polymorphs I and III and its reversion after boiling in water

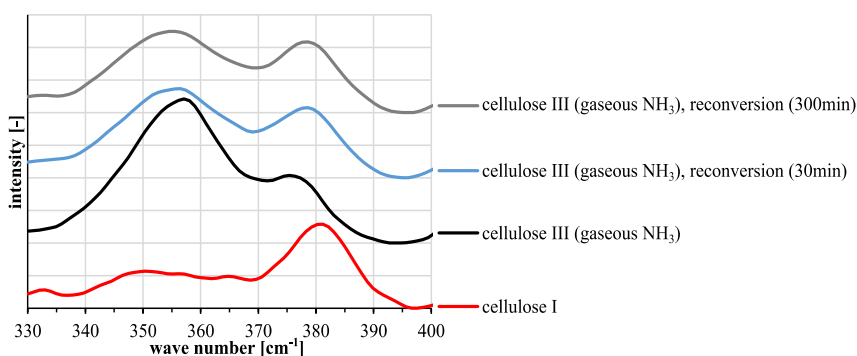


Figure 6: Raman spectrograms of cellulose polymorphs I and III and its reversion after boiling in water

In order to achieve a complete reversion, it would be possible to lower the pH value by adding an acid. Alternatively, increasing the treatment temperature should also favour complete reversion.¹⁶

Furthermore, there are two important changes that must be taken into account in the reversion of the cellulose: cellulose III is only

converted back to cellulose I_β, because this is the thermodynamically more stable form of cellulose I.¹⁷ Native cellulose I_α is thus converted to cellulose I_β. Secondly, cellulose III is crystallographically, but not morphologically transformed into cellulose I, which is accompanied by a reduction in crystallinity.⁹

CONCLUSION

Ammonia treated dissolving pulp was analysed using X-ray diffraction and Raman spectroscopy. The study revealed a distinct change in the crystal structure of cellulose I to cellulose III. Since the conversion of cellulose occurred above a certain pressure level, a direct pressure dependence could be determined. A catalytic effect of water was detected, as its presence had lowered this pressure level. However, the reconversion of cellulose III to I did not occur, as expected according to the literature, which is therefore subject to further investigation.

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