



<http://www.diva-portal.org>

## Postprint

This is the accepted version of a paper published in *Cellulose (London)*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Albán Reyes, D C., Skoglund, N., Svedberg, A., Eliasson, B., Sundman, O. (2016)  
The influence of different parameters on the mercerisation of cellulose for viscose  
production  
*Cellulose (London)*, 23(2): 1061-1072  
<https://doi.org/10.1007/s10570-016-0879-0>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-119633>

# THE INFLUENCE OF DIFFERENT PARAMETERS ON THE MERCERISATION OF CELLULOSE FOR VISCOSE PRODUCTION

Diana Carolina Albán Reyes<sup>1</sup>, Nils Skoglund<sup>1,2</sup>, Anna Svedberg<sup>3</sup>, Bertil Eliasson<sup>1</sup>, Ola Sundman<sup>1</sup>

<sup>1</sup>Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden.

<sup>2</sup>Department of Engineering, Science and Mathematics, Luleå University of Technology, SE-971 87 Luleå, Sweden

<sup>3</sup>Domsjö Fabriker AB, SE-891 86 Örnsköldsvik, Sweden.

Corresponding author: Ola Sundman, [ola.sundman@umu.se](mailto:ola.sundman@umu.se), tel: +46907866072

## Acknowledgements

Industrial Doctoral School at Umeå University, Domsjö Fabriker AB, AkzoNobel Functional Chemicals AB, Bio4Energy and The Royal Swedish Academy of Agriculture and Forestry are all acknowledged for financial support. András Gorzsas at the Vibrational Spectroscopy platform at KBC (Umeå University) is acknowledged for experimental guidance and help.

## Abstract

A quantitative analysis of degree of transformation from a softwood sulphite dissolving pulp to alkalisated material and the yield of this transformation as a function of the simultaneous variation of the NaOH concentration, denoted [NaOH], reaction time and temperature was performed. Samples were analysed with Raman spectroscopy in combination with multivariate data analysis and these results were confirmed by X-ray diffraction. Gravimetry was used to measure the yield. The resulting data were related to the processing conditions in a Partial Least Square regression model, which made it possible to explore the relevance of the three studied variables on the responses. The detailed predictions for the interactive effects of the measured parameters made it possible to determine optimal conditions for both yield and degree of transformation in viscose manufacturing. The yield was positively correlated to the temperature from room temperature up to 45 °C, after which the relation was negative. Temperature was found to be important for the degree of transformation and yield. The time to reach a certain degree of transformation (i.e. mercerisation) depended on both temperature and [NaOH]. At low temperatures and high [NaOH], mercerisation was instantaneous. It was concluded that the size of fibre particles (mesh range 0.25 mm - 1 mm) had no influence on degree of transformation in viscose processing conditions, apparently due to the quick reaction with the excess of NaOH.

## Keywords

Mercerisation. Cellulose I. Cellulose II. Raman spectroscopy. X-ray diffraction patterns. Multivariate data analysis.



## Introduction

A global population growth and increasing prosperity pushes the demand for textile fibre, while environmental constraints and climate change is limiting market growth for cotton and fossil-based synthetic fibres (Hämmerle 2011; Novotny and Nuur 2013). Viscose rayon, a fibre based on regenerated cellulose, is a sustainable alternative textile fibre material which has many applications including spun yarn, fabrics, and textiles (Novotny and Nuur 2013; Shen et al. 2010; Grand View Research June 2014). The first step in modifying dissolving pulp with cellulose I (Cell I) into viscose is an alkali treatment, typically performed with NaOH, called mercerisation. During this treatment the Cell I in the dissolving pulp transforms into a reactive and highly swollen material called alkali cellulose (Na-Cell) where the molecular structure of the cellulose is more accessible to chemical reagents.

This change has been extensively studied as a function of temperature and [NaOH]. Older literature refers to five different forms of crystalline Na-Cell occurring as intermediates during the mercerisation (Sobue and Kiessig 1939). More recently Porro et al. (2007) suggested a reconsideration of the definition of the Na-Cell complex. By using  $^{13}\text{C}$  CP/MAS NMR experiments, it was found that only two stable forms, labelled Na-Cell I and Na-Cell II, could be distinguished within the phase diagram.

It is well-recognized that Na-Cell turns into antiparallel glucoside chains in the crystalline form of cellulose II (Cell II) upon drying after the NaOH has been washed out of the cellulose structure (Langan et al. 2001; Okano and Sarko 1985). However, if the wash is done at high temperatures (i.e. 85 °C) Na-Cell I can transform into the parallel Cell I polymorph instead (Sisson and Saner 1941; Takahashi and Takenaka 1987). Research has tended to focus on transformation of Cell I to Cell II via the mercerisation process in order to reveal the mechanisms of mercerisation. Sisson and Saner (1941) presented qualitative diagrams of three degrees of transformation (DoT) (native cellulose, partially mercerised and fully mercerised) as a function of temperature from -20 °C to 100 °C and [NaOH] from 2% to 50% using X-ray diffraction. More recently, Borysiak and Garbarczyk (2003) studied quantitatively the DoT from Cell I to Cell II only as a function of the [NaOH] in an interval from 10% to 25% and reaction time from 1 minute to 30 minutes using WAXS. Later, Schenzel et al. (2009) developed a calibration model based on FT Raman spectroscopy to evaluate the DoT. In that paper, the DoT to Cell II via mercerisation of sulphite pulp as a function of the [NaOH] from 2% to 28% was investigated quantitatively.

Mercerisation is, consequently, a well-studied area in which a considerable number of studies have been conducted. However, in most of the mention studies the authors have focused on only two variables; in no study reaction time, temperature and [NaOH] have all been co-varied and the DoT quantitatively analysed. Furthermore, in none of the mentioned studies the yield of the cellulose had been considered together with DoT to Cell II. Simultaneous optimization of both DoT and yield in the mercerisation process at viscose

production conditions as a function of reaction time, temperature and [NaOH] had to our knowledge not been presented.

The aim of the present study was to improve the understanding of the mercerisation of softwood sulphite dissolving pulp in industrially relevant conditions for production of viscose fibres, to suggest optimum mercerisation conditions based on the parameters in this study, and to investigate the influence of grinding size of softwood sulphite dissolving pulp on the rate of mercerisation. This was achieved by quantitative analysis of both the DoT and mass yield as a function of simultaneous variation of [NaOH], temperature, and reaction time. A combination of Raman spectroscopy and multivariate data analysis has been used to study the DoT. X-ray diffraction patterns were used to confirm the structures in the calibration curve and to qualitatively study the changes of the structure during the transformation. The yield was measured from the difference in mass before and after mercerisation. Mannose and xylose content in some mercerised samples were used to study the change in hemicellulose content. This approach provided extensive information that could be used to better understand the mechanism of mercerisation.

## Materials and methods

### Materials

The native starting material containing Cell I was a sulphite dissolving cellulose pulp from a blend of softwood, spruce and pine, provided by Domsjö Fabriker AB, Örnsköldsvik, Sweden. It had a molecular weight of  $3.92 \times 10^5 \text{ g mol}^{-1}$  (KA 10.312), a viscosity of  $544 \text{ ml g}^{-1}$  (ISO 2470:1999), R 18 value of 95.3 % (ISO 699:1982) and R 10 value of 89.6 % (ISO 699:1983). The NaOH (ACS reagent,  $\geq 97.0\%$ , Sigma Aldrich) was used without any further purification. Deionised  $\text{H}_2\text{O}$  was used for washing the mercerised samples. Degassed (by boiling) ultrapure Milli-Q  $\text{H}_2\text{O}$  was used for preparation of all alkaline solutions. The solutions were prepared in a thermostatted room at  $25 \pm 0.1 \text{ }^\circ\text{C}$  and used within a week.

### Experimental design for the mercerisation of samples

Reaction time (t), temperature (T) and [NaOH] were chosen as parameters in this study since these were easily varied both industrially and in the laboratory, and results produced could be compared with previous studies. The levels of the parameters used in viscose productions were collected from industrial partners and verified with literature (Mozdyniewicz et al. 2013). The experimental range for these three variable parameters was chosen based on the suggested levels. Additionally, the grinding size was chosen as a fourth parameter to investigate whether it would influence mercerisation.

Set 1: The experimental design consisted of simultaneous variation of all three parameters. The initial design consisted of the variation of three lengths of time; 600 seconds, 2100 seconds, and 3600 seconds, three levels of temperature;  $20 \text{ }^\circ\text{C}$ ,  $35 \text{ }^\circ\text{C}$ , and  $50 \text{ }^\circ\text{C}$  and three levels of [NaOH];  $4.4 \text{ mol/dm}^3$  (15 w/w %),  $5.5 \text{ mol/dm}^3$  (18 w/w %), and  $6.6 \text{ mol/dm}^3$  (21 w/w %). The two responses were DoT (from Cell I to Cell

II) and mass yield. The experimental design was derived using MODDE software v.9.1.1.0 (Umetrics AB, Umeå, Sweden). A central composite face (CCF) design (Eriksson 2008), and quadratic model was applied. The initial experimental design consisted of 14 experiments augmented with three replicates of the central points. This design was later expanded with 14 additional experiments (c.f. Table 1 for details).

Set 2: The experiments consisted of variation of grinding size (0.25 mm, 0.5 mm, 1 mm mesh size), and reaction time (60 seconds, 600 seconds, 2100 seconds, and 3600 seconds). [NaOH]: 5.5 mol/dm<sup>3</sup> (18 w/w %), and temperature 35° C were kept constant at the central points. The experimental response was the DoT to Cell II. A total of 12 experiments plus replicates were carried out.

### **Sample preparation**

The starting material was ground in a Retsch Ultra Centrifugal Mill ZM 200. The grinding size used as starting material for both the calibration set and set 1 was 0.5 mm mesh size. For set 2, the grinding sizes were as given above.

### **Calibration set samples**

To obtain a “fully” transformed Cell II material the dissolving cellulose pulp was dispersed in 30% NaOH solution at 3 °C for one hour and then kept still at room temperature for 24 h. The resulting mercerised sample was washed to neutral pH with deionised H<sub>2</sub>O and dried until constant weight at 40 °C in vacuum. After this procedure the sample was considered to be transformed into Cell II and amorphous cellulose. In order to create a calibration set starting material and “fully” transformed Cell II were mixed in different proportions (w/w) as described by Schenzel et al. (2009). The mixtures ranged from pure starting material to pure “fully” transformed Cell II material in steps of 10 % (w/w). The mixtures were then suspended in deionised water and mixed with a stirrer for five days in order to get a more homogenous blend. The samples were then dried at 40 °C in vacuum until constant weight.

### **Mercerisation of samples**

To mimic viscose processing conditions, mercerisation was performed at 5% (w/v) cellulose content. NaOH solution was added to ground starting material in a jacketed glass vessel. To stop the reaction the [NaOH] was quickly brought to below 5% by addition of deionised H<sub>2</sub>O and the samples were washed with excess of deionised water to neutral pH. Samples were then dried until constant weight at 40 °C in vacuum. The yield of the reaction for set 1 was calculated by measuring sample weight before and after the mercerisation.

### **Raman spectroscopy**

Raman spectroscopy mapping of thin and flat surfaces of the samples were recorded with a Renishaw InVia Raman spectrometer equipped with a CCD detector. A 785 nm infrared diode laser and a maximum power of 300 mW was used. The measurements were performed in static mode centred at 950 cm<sup>-1</sup> (328-1496 cm<sup>-1</sup>

<sup>1</sup>) using 1200 lines grating. The image step size was 10 microns, using a 20x lens. Between 90 and 226 spectra were recorded for every image. The pixels were filtered from cosmic rays using WiRE (version 3.0, Renishaw Plc, UK), baseline corrected and standardized using the Matlab script provided by Felten et al. (2015). The lambda used was 100, and p value 0.001. An average spectrum was then calculated for each sample.

### **X-ray diffraction measurements**

Powder X-ray diffraction (XRD) was used to determine the crystalline content and DoT to Cell II for the starting material, 50/50 blend, “fully” transformed Cell II material and selected samples from the experimental design. The starting material sample was pressed into a disk with 1 mm thickness prior to analysis which ensured a flat analysis surface suitable for XRD measurements. This sample was then mounted on a standard plastic sample holder containing rutile, which was later observed in the analysis. The mercerized samples, partly and completely, were pressed into thinner tablets and analysed on a Si single crystal sample holder to avoid adding the mentioned rutile peaks. The sample preparation method, which uses pressure for smooth sample surfaces, may have caused slight unit cell changes due to straining effects. However, since any imposed shifts will affect the entire cellulose patterns it was expected that qualitative and quantitative analysis would be possible for the mercerised samples by using proper unit cell modifications for the pure Cell I and Cell II references.

Diffraction data was collected using continuous scans and a rotating sample stage on a Bruker D8Advance instrument in  $\theta$ - $\theta$  mode with a line-focused Cu-K $\alpha$  radiation source, 1.0 mm fixed divergence slit, and a Våntec-1 detector. The data collected was analysed qualitatively using Difffrac.EVA (DIFFRAC.EVA 3.2 2014) and quantitatively using Rietveld refinement in Difffrac.Topas v4.2 (Difffrac<sup>plus</sup> TOPAS 4.2 2009). The reference structure used in quantification of Cell I was published by Nishiyama et al. (2002), available in the Cambridge crystallographic database as cellulose I $\beta$  with the reference code JINROO01. French (2014) provided the reference structure for cellulose II based on the structure determined by Langan et al. (2005).

### **Carbohydrate composition**

The method used in this study was based on the carbohydrate analysis by ion chromatography reported by Suzuki et al. (1995). The moisture content of the selected samples (cf. online resource) were measured using a Mettler Toledo HG63 moisture analyser, in order to calculate the dry weight of the samples. 0.1 g of the samples were placed in a glass tube and 3 ml of 72% (w/w) H<sub>2</sub>SO<sub>4</sub> solution was added. Hydrolysis was performed for 1 h at 30 °C in a water bath. The hydrolysed samples were diluted with deionized water to 2.5 % H<sub>2</sub>SO<sub>4</sub> and autoclaved at 120 °C for 1 h. After this, the samples were diluted 100 times and levels of

the sugars were determined using Dionex ICS-3000 Ion Chromatography System equipped with a CarboPac PA20 (3 × 30 mm). Results are shown in the online resource (Fig. S4).

## **Multivariate data analysis**

Multivariate analysis of the averaged spectral mapping data of the samples was performed in SIMCA v.13.0.3.0 (Umetrics AB, Umeå, Sweden). Partial least square (PLS) regression method (Eriksson et al. 2013; Geladi and Kowalski 1986) was used to correlate variation in the spectral data to the levels of starting material and Cell II in the samples using mean-centering scaling on the spectral data. The DoT in the mercerised samples were then predicted using the calibration model.

PLS analysis was also performed to relate reaction time, temperature and [NaOH] during the mercerisation to the predicted DoT and yield (%) for the mercerised samples. Unit variance scale was used in this analysis.

## **Results and discussion**

### **Raman spectroscopy for cellulose I and cellulose II**

The technique to quantify the DoT from the softwood sulphite dissolving pulp to “fully” transformed Cell II material in this study was based on the Raman spectra studies on Cell I and Cell II published by Atalla (1975) and Schenzel et al. (2009). The technique allows distinguishing between Cell I and II by using the whole spectra profile of samples at wavenumbers between 1500 cm<sup>-1</sup> and 150 cm<sup>-1</sup>. The distinction was explained by different conformations of molecular chains in the two crystalline structures. The structure shown in Fig. 1 is Cell I $\beta$  which is present in native lignocellulosic materials (Nishiyama et al. 2002), here plotted using Mercury 3.6 (Macrae et al. 2008). The Raman lines characteristic of these structures, together with the corresponding loadings generated by the first component ( $R^2 > 98\%$ ) in the calibration model developed in this study, are illustrated in Fig. 2. Raman spectra were interpreted by comparison with Wiley and Atalla (1987), Schenzel and Fischer (2001), Fischer et al. (2005), and Schenzel et al. (2009).

The typical band at 1477 cm<sup>-1</sup> in the Raman spectra for Cell I indicated the simultaneous presence of two stereochemical non-equivalent CH<sub>2</sub>OH groups, resulting from the rotation of the side chains about the C-5 and C-6 atoms. During the transition to Cell II, only one type of CH<sub>2</sub>OH was reported (Fischer et al. 2005). This was seen as a correlation for the loadings with Cell I (positive peak) at 1477 cm<sup>-1</sup> and this signal was shifted to approximately 1464 cm<sup>-1</sup> for Cell II (negative peak). The band at 1267 cm<sup>-1</sup> in Cell II was attributed to the twisting mode of the methylene groups (Schenzel et al. 2009). The wavenumbers between 1150 and 1270 cm<sup>-1</sup> have been identified as a transition region and attributed to the vibrational modes involving significant amounts of skeletal stretching, and methine bending vibrations (Schenzel and Fischer 2001).

The band at  $895\text{ cm}^{-1}$  in Cell I shifted to  $897\text{ cm}^{-1}$  for Cell II, which was comparable to the spectral resolution and thereby experimental error. It was assigned to HCC and HCO bending localized at C-6 atoms (Wiley and Atalla 1987). However, the band for Cell II was more intense, and the loading plot therefore shows a strong correlation with this polymorph; the intensity of this band was attributed to the amount of disorder in the cellulose structure (Wiley and Atalla 1987). As also can be observed in the loading line, the bands at  $577\text{ cm}^{-1}$ , and at  $421\text{ cm}^{-1}$  were correlated to Cell II while the double band at  $459\text{ cm}^{-1}$  and  $438\text{ cm}^{-1}$  was only seen in Cell I. Schenzel et al. (2009) described that the intensity of band at  $380\text{ cm}^{-1}$  decreases and the intensity increases at band  $355\text{ cm}^{-1}$  during the transition from Cell I to Cell II.

### **X-Ray diffraction measurements**

The sample preparation method used for the calibration model was evaluated by XRD analysis of three samples that were prepared to contain pure starting material (Cell I polymorph), 50 w/w-% starting material and 50 w/w-% “fully” transformed Cell II material, and pure “fully” transformed Cell II. The average diffractogram for the 50/50-sample was compared with the analyses of the pure samples. The resulting normalized diffractograms suggest that the blending of the two materials worked well (c.f. Fig. 3) and subsequent Rietveld refinement indicated that the ratio of the crystalline polymorphs were 50.5% Cell I and 49.5% Cell II.

The peaks produced primarily by Cell II in the mercerised samples are much broader than what was observed for the idealized diffractograms produced by French (2014) using theoretical modelling. Compared to the work by French (2014) the peak maximum positions are shifted slightly and there may be a preferred orientation along the fibre axis for Cell II. These positional differences are largely attributed to small variations in the unit cell but may indicate some content of Cell I. Unfortunately, the peak broadening in the diffractograms shown in Figure 4 lead to inconclusive results from Rietveld refinement using both Cell I and Cell II. In addition to a small average crystallite size (inconclusive models suggest a Lorentzian volume integral breadth around 3.5 nm or less) which caused extensive peak broadening, there may have been some contribution from Cell I as indicated by the slight peaks at  $2\theta\ 16^\circ$  which Cell II should not display as well as amorphous scattering from non-crystalline material. The total contribution from these features could not be successfully resolved to estimate the relative content of Cell I and Cell II or provide reliable models for unit cell dimensions.

The largest difference between the samples can be seen for sample preparation temperatures from  $50^\circ\text{C}$  and up (samples #17 to #28 in Fig. 4), where the (020)-reflection becomes more dominant than the (110)-reflection. The higher background between the two dominating peaks seen for samples #26 and #28 is not accompanied by a strong peak at  $2\theta\ 14^\circ\text{--}17^\circ$ , as would be expected with a significantly higher Cell I content. Still, the data in Figure 4 suggest that the higher process temperature may impact the quality of the Cell II produced, since features from other sources than Cell II affect the diffractograms.



## **Multivariable calibration model on Raman spectra of cellulose I and II**

A PLS analysis method was performed on the averaged Raman spectral mapping data of the 9 calibration set samples. Thus a PLS model was obtained that allows the quantification of the DoT from the starting material (Cell I) to “fully” transformed Cell II material (i.e. Cell II). The DoT was expressed as (Cell II/(Cell I+II)). The model obtained explained 99 % and predicted 98% of the variation in DoT, c.f. Fig. 5.

The calibration model developed was then used to predict the DoT of the starting material to “fully” transformed Cell II material in the mercerised samples, by using the whole average spectral mapping data for each sample. As seen in Table 1 the values for the three replicate samples were similar. Hence, the reproducibility of the measurements was high. Furthermore, the DoT data from Raman spectroscopy and PLS (Table 1) agree with the DoT observed in the X-ray diffractograms (Fig. 4). It should be noted, however, that some samples show slight deviations from the general behaviour. Since the model is evaluated over the whole data range it shows only the common behaviour of data.

## **Influence of the grinding size on the degree of transformation**

To study the influence of grinding size on the DoT under mercerisation in viscose manufacturing conditions, starting material was ground at 0.25 mm, 0.5 mm and 1.0 mm mesh. Samples were mercerised at constant temperature and [NaOH]. The results showed no significant difference in reaction time depending on mesh size, i.e. the grinding size showed no influence on DoT under the used mercerisation conditions. The mesh sizes used, 0.25-1.0 mm, result in small fibre particles which react easily with the excess of NaOH solution during the mercerisation.

## **Partial least squares analysis on the degree of transformation and yield**

A PLS analysis was performed to relate reaction time, temperature and [NaOH] during the mercerisation to DoT (%) and yield (%) for mercerised samples. Preliminary data analysis revealed a non-linearity between temperature (T) and the yield. Therefore it was found necessary to expand the variables mentioned above with a complementary model term, temperature square ( $T^2$ ). It was found that using these four variables was the best combination for explaining the two responses simultaneously. From this a PLS-model was developed using two components. This model could explain 70% and predict 56% of the variation in the data. The CV-ANOVA for the overall model reported p-values of less than 0.05, (yield 4.282E-04 and Cell II 2.051E-04). As can be seen in Table 1 many data points are tightly clustered and those that differ distinctly can be found at higher temperatures and shorter times. The three replicates of the centre point showed only small variation, indicating that the error in the measurements were small and that variation between samples were significant. The variable importance plot (Fig. 6) and coefficient plot (Fig. 7) are presented with 95% confidence level. Figure 6 shows that all the variables contribute to the model, but that the order of their importance cannot be statistically determined.

The interactive effects of the three parameters on the DoT (Fig. 7a) show that temperature had the largest influence, correlating negatively with the DoT. As an example, the DoT decreases from 96 % to 84 % by changing temperature from 20 °C to 70 °C (samples #3 and #28 respectively). In the model [NaOH] had a positive influence on the DoT but in the data it can only be observed at temperatures over 40-50 °C. By increasing [NaOH] from 15 % to 21% at 70 °C the achieved DoT increases significantly, from 84 % to 94 % (samples #28 and #30). Sisson and Saner (1941) indicated a negative influence of temperature on the DoT. They concluded that increased temperature displaces the reaction maximum to higher [NaOH], which was in agreement with our model. It can also be observed that increased reaction time had no significant influence on the modelled DoT over all samples.

The mercerisation reaction occurred quickly at low temperature and thus transformation to Cell II was completed within a few minutes (Sisson and Saner 1941; Borysiak and Garbarczyk 2003). A high DoT (99%) was also obtained in only 45 seconds (sample #1). However, the dependence of time was affected by temperature and [NaOH] as can be seen in Table 1 and Fig. S1 (online resource). In our experiments, reactions at high temperatures occur slower and were therefore more affected by time. Our data show that at high temperature long reaction time was necessary to increase the DoT. With the same [NaOH] and temperature, a prolonged reaction time from 600 seconds to 3600 seconds resulted in an increase of the DoT from 84 to 93% (samples #28 and #29 respectively). As this result is contrary to chemical intuition, it deserves a short explanation. It is well known that cellulose fibres during NaOH treatment swell more at low temperature (*e.g.* room temperature) than at elevated (*e.g.* 70 °C) temperature, because of the negative enthalpy of the swelling reaction. Therefore, the accessibility of the cellulose for the NaOH was lower at higher temperature, decreasing the reaction rate. In this study full DoT was never reached at 70 °C. Sisson and Saner (1941), however, showed that complete mercerisation could be reached at 75 °C and 25 % [NaOH] in samples measured after two weeks of mercerisation. When a sample with the same parameters was run in a nitrogen atmosphere, full DoT was not achieved. Therefore, the authors suggested that what looks like a continued mercerisation more likely was a degrading effect of NaOH on cellulose in the presence of O<sub>2</sub> which caused a more accessible structure.

The data showed that prolonged reaction time had a negative influence on the yield, which can also be seen in the model (Fig. 7b). When the reaction time was extended from 600 second to 3600 seconds at 70°C and 21% [NaOH], for example, the yield decreased from 88.5 to 84.9% (samples #30 and #31 respectively). The effect of temperature was non-linear and was well modelled with an expanded quadric term ( $T^*T$ ). A comparison of samples produced at 20 °C, 50 °C and 70 °C shows that the yield increased from 87.7 to 91.1% with the first temperature increase, but then decreased to 86.4 % for the highest temperature (samples #4, #20 and #29 respectively). This kind of dependence of temperature can possibly be explained by how cellulose fibres respond to low and high temperatures respectively. It was well known that the swelling of

cellulosic fibres increase at low temperature, which facilitated dissolution of short chained material during alkali treatment (Sixta 2008). This could explain the low yield at room temperature, since a larger amount of fine material was thus free and could pass through the filter during washing. Sixta (2008) and Syed et al. (2013) mentioned that the alkali caused peeling reactions (Fig. 8) that lead to degradation of pulp carbohydrates at high temperatures and low [NaOH]. This might explain why our data shows that yield decreases with temperatures above approximately 50 °C. In the current study the modelled yield was maximised at about 45 °C. In the model, [NaOH] showed no significant influence on the yield. However, an often used fact for quality control in the industry is that 10% of NaOH dissolve both hemicellulose and short chain cellulose, while 18% NaOH only dissolve the hemicelluloses (Sixta 2008). Therefore, a positive co-variation between the [NaOH] and yield was expected. Instead, no significant effect could be seen at room temperature. Only a minor negative effect can be seen in the data at temperatures between 35 and 60 °C. As an example, at 35 °C and 2100 seconds, increased [NaOH] from 15 to 21% only decreased the yield from 89.7 to 88.8% (samples #10 and #16 respectively) which is not a significant decrease.

The PLS analysis presented in this study allowed us to further explore the influence of the three studied variables on the modelled responses. For that purpose, response contour plots for the DoT (Fig.9) and yield (Fig. 10) were generated with constant reaction time and [NaOH] respectively. The quantification of the DoT and yield was important for multivariable modelling, e.g. to optimisations. The results shows that reaction time had a negative influence on yield and non-significant influence on DoT in the model. Hence contour plots with constant time at 45 seconds (Fig. 9a and Fig. 10a) were created. Since [NaOH] had positive influence on Cell II content and no significant effect on yield 21 % [NaOH] was selected as a constant variable to generate response contour plots Fig. 9b and Fig. 10b. The observable similarities between these models and the data plots (Fig. S1, and Fig. S2 in the online resource) show that the model can predict the trends in the data well, which supports the conclusions drawn from the models.

The response contour plots for the modelled DoT (Fig. 9) were designed on the assumption that mercerisation is performed with the purpose of reaching full DoT. A modelled DoT over 98 % was defined as full transformation. Fig. 9a depicts the interdependence of [NaOH] and temperature at 45 seconds. In this study, full conversion could be reached in a temperature span from 20°C to 29 °C, at a time-dependent minimum [NaOH]; the minimum [NaOH] at 20 °C was 18.7 % and increased to 21 % at 29 °C. The modelled interdependence of time and temperature at 21 % [NaOH] is plotted in Fig. 9b. As discussed previously the influence of time was dependent on temperature. At higher temperatures, longer reaction times were necessary for higher DoT. Fig. 9b show that, according to this model, full conversion with 21% [NaOH] was reached within 45 seconds at temperatures below 29°C, which increased to 3600 seconds at 50 °C.

In Fig. 10 the modelled yield is presented as function of the same parameters as the DoT in Fig. 9. Optimum yield was herein defined as retention above 90 %. As discussed previously, the yield showed a

non-linear dependence of the temperature. A quadratic dependence of the temperature was found to fit well with the data (Fig. 10, and Fig. S2 in the online resource for comparison). In the model, yield had a positive correlation with temperature until 45 °C, after which the relationship was negative. As mentioned previously the explanation of this behaviour at low temperature (e.g. 20 °C) was attributed to increased swelling of the fibre, allowing more material to dissolve. At high temperature (e.g. 70 °C) peeling reactions dominate the yield loss. Fig. 10a shows that optimum yield could be achieved at the low end of measured temperature range (20 °C to 24 °C) at [NaOH] lower than 17.5 % and 21% respectively. At the high end of the measured range (66 °C to 70 °C) optimum yield was reached at [NaOH] lower than 21 % to 17.5 % respectively. According to Fig. 10b, optimum yield could be achieved at 21 % [NaOH] in a temperature span from 24 °C to 66 °C given a maximum time. At 24 °C and 66 °C the maximum time was within 45 seconds and about 2000 seconds at 45 °C.

Optimal conditions in the model plots (Fig. 9 and Fig. 10) were the areas where full DoT to Cell II (Cell II >98%) could be achieved with optimum yield (>90%). According to the model, both requirements could be met in a temperature span from 24-29 °C at 21 % [NaOH] and a reaction time of 45 seconds. The highest possible yield within this span was achieved at 29 °C. As can be seen by combining Fig. 9 and Fig. 10, similar results could be achieved at other conditions as well. But, at increased temperatures and prolonged reaction times, as well as at lower [NaOH], the area of optimal conditions for both DoT and yield decreased. The best conditions for a high degree of mercerisation as well as yield was mathematically calculated with the computer program MODDE software v.10.1 (Umetrics AB, Umeå, Sweden). The optimum point found was 29 °C, 45 seconds and 21 % [NaOH] which are the same values as from the manual optimisation. For industrial applications the time consumption of any process step is vital. Therefore it was interesting that the mercerisation was instantaneous at room temperature, but that the reaction was slowed down at higher temperatures. However, in our study we see that the yield was highest at approximately 45-50 °C, which might also be relevant for the industrial process. The compromise to reach optimal mercerisation conditions found in this investigation show that the temperature used industrially could be modified, that the time necessary for mercerisation hence would decrease. The details of the optimisation are found in the online resource (Fig. S3).

It should be noted that both DoT and yield depend on the interactive effect of all parameters. Thus, the optimum mercerisation conditions were co-dependent of time, [NaOH], and temperature.

## Conclusions

A multivariate approach was successfully applied to describe the co-dependencies of some variables possible to control during mercerisation. The temperature was found to be important by itself, contributing to the DoT (linear dependence) and yield (non-linear dependence). The DoT showed a clear decrease with increasing temperature between 20 and 70 °C. Highest possible yield was found at approximately 45-50 °C.

[NaOH] and reaction time showed a more complicated behaviour and should be analysed in the light of the other variables. The optimum point for both DoT and yield in this study was found to be 29 °C, 45 seconds and 21 % [NaOH].

## References

- Atalla RH (1975) Raman spectral studies of polymorphy in cellulose. Part 1, Celluloses I and II.
- Borysiak S, Garbarczyk J (2003) Applying the WAXS method to estimate the supermolecular structure of cellulose fibres after mercerisation. *Fibres Text East Eur* 11 (5):104-106
- DIFFRAC.EVA 3.2 (2014). Bruker AXS GmbH, Karlsruhe, Germany,
- Diffra<sup>plus</sup> TOPAS 4.2 (2009). Bruker AXS GmbH, Karlsruhe, Germany,
- Eriksson L (2008) Design of experiments: principles and applications. MKS Umetrics AB,
- Eriksson L, Byrne T, Johansson E, Trygg J, Vikström C (2013) Multi-and megavariate data analysis basic principles and applications. Umetrics Academy,
- Felten J, Hall H, Jaumot J, Tauler R, de Juan A, Gorzsas A (2015) Vibrational spectroscopic image analysis of biological material using multivariate curve resolution-alternating least squares (MCR-ALS). *Nature Protocols* 10 (2):217-240. doi:10.1038/nprot.2015.008
- Fischer S, Schenzel K, Fischer K, Diepenbrock W (2005) Applications of FT Raman spectroscopy and micro spectroscopy characterizing cellulose and cellulosic biomaterials. *Macromolecular Symposia* 223:41-56. doi:10.1002/masy.200550503
- French AD (2014) Idealized powder diffraction patterns for cellulose polymorphs. *Cellulose* 21 (2):885-896. doi:10.1007/s10570-013-0030-4
- Geladi P, Kowalski BR (1986) Partial least-squares regression: a tutorial. *Analytica Chimica Acta* 185:1-17. doi:[http://dx.doi.org/10.1016/0003-2670\(86\)80028-9](http://dx.doi.org/10.1016/0003-2670(86)80028-9)
- Grand View Research I (June 2014) Cellulose Fibers Market Analysis By Application (Spun Yarn, Fabrics, Clothing and Other) And Segment Forecasts To 2020. <http://www.grandviewresearch.com/industry-analysis/cellulose-fibers-market>. Accessed 2/4/2015
- Hämmerle FM (2011) The cellulose gap. *Lenzing Ber* 89:12-21
- Langan P, Nishiyama Y, Chanzy H (2001) X-ray Structure of Mercerized Cellulose II at 1 Å Resolution. *Biomacromolecules* 2 (2):410-416. doi:10.1021/bm005612q
- Langan P, Sukumar N, Nishiyama Y, Chanzy H (2005) Synchrotron X-ray structures of cellulose I-beta and regenerated cellulose II at ambient temperature and 100 K. *Cellulose* 12 (6):551-562. doi:10.1007/s10570-005-9006-3
- Macrae CF, Bruno IJ, Chisholm JA, Edgington PR, McCabe P, Pidcock E, Rodriguez-Monge L, Taylor R, Streek Jvd, Wood PA (2008) Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures, . *J Appl Cryst* 41:466-470
- Mozdyniewicz DJ, Nieminen K, Sixta H (2013) Alkaline steeping of dissolving pulp. Part I: cellulose degradation kinetics. *Cellulose* 20 (3):1437-1451. doi:10.1007/s10570-013-9926-2
- Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in cellulose I beta from synchrotron X-ray and neutron fiber diffraction. *J Am Chem S* 124 (31):9074-9082. doi:10.1021/ja0257319
- Novotny M, Nuur C (2013) The transformation of pulp and paper industries: the role of local networks and institutions. *International Journal of Innovation and Regional Development* 5 (1):41-57
- Okano T, Sarko A (1985) Mercerization of cellulose. II. Alkali-cellulose intermediates and a possible mercerization mechanism. *J appl polym sc* 30 (1):325-332. doi:10.1002/app.1985.070300128
- Porro F, Bedue O, Chanzy H, Heux L (2007) Solid-state C-13 NMR study of Na-cellulose complexes. *Biomacromolecules* 8 (8):2586-2593. doi:10.1021/bm0702657

- Schenzel K, Almlöf H, Germgård U (2009) Quantitative analysis of the transformation process of cellulose I -> cellulose II using NIR FT Raman spectroscopy and chemometric methods. *Cellulose* 16 (3):407-415. doi:10.1007/s10570-009-9286-0
- Schenzel K, Fischer S (2001) NIR FT Raman spectroscopy - a rapid analytical tool for detecting the transformation of cellulose polymorphs. *Cellulose* 8 (1):49-57. doi:10.1023/a:1016616920539
- Shen L, Worrell E, Patel MK (2010) Environmental impact assessment of man-made cellulose fibres. *Resources, Conservation and Recycling* 55 (2):260-274. doi:<http://dx.doi.org/10.1016/j.resconrec.2010.10.001>
- Sisson WA, Saner WR (1941) The Effect of the Temperature and the Concentration of Sodium Hydroxide on the X-ray Diffraction Behavior of Raw and of Degraded Cotton. *The Journal of Physical Chemistry* 45 (5):717-730. doi:10.1021/j150410a001
- Sixta H (2008) Pulp Purification. In: *Handbook of Pulp*. Wiley-VCH Verlag GmbH, pp 933-965. doi:10.1002/9783527619887.ch8
- Sobue H, Kiessig H (1939) The Cellulose-sodium Hydroxide-water System as a Function of the Temperature. *Z Physikal Chem B* 43:309-328
- Suzuki M, Sakamoto R, Aoyagi T (1995) RAPID CARBOHYDRATE ANALYSIS OF WOOD PULPS BY ION CHROMATOGRAPHY. *Tappi J* 78 (7):174-177
- Syed HU, Nebamoh IP, Germgård U (2013) A comparison of cold and hot caustic extraction of a spruce dissolving sulfite pulp prior to final bleaching. *Appita J* 66 (3):229-234
- Takahashi M, Takenaka H (1987) Transition from Cellulose I Family to Cellulose II Family. *Polym J* 19 (7):855-861. doi:10.1295/polymj.19.855
- Wiley JH, Atalla RH (1987) BAND ASSIGNMENTS IN THE RAMAN-SPECTRA OF CELLULOSES. *Carbohyd Res* 160:113-129. doi:10.1016/0008-6215(87)80306-3