



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

This is the published version of a paper presented at *4th EPNOE International Polysaccharide Conference "Polysaccharides and polysaccharide-based advance materials: from science to industry". 2015, Warsaw, Poland.*

Citation for the original published paper:

Albán Reyes, D C., Sundman, O., Schröder, U., Karlsson, L., de Wit, P. et al. (2015)
Activation of dissolving cellulose pulp at low water content
In: *4th EPNOE International Polysaccharide Conference: Polysaccharides and polysaccharide-based advance materials: from science to industry*

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-128509>

Albán Reyes Diana Carolina ¹, Sundman Ola ¹, Schröder Ulf ², Karlson Leif ², de Wit Paul ³, Eliasson Bertil ¹
¹Department of chemistry, Umeå University, SE-901 87 Umeå, Sweden. ²AkzoNobel, SE-444 85 Stenungsund, Sweden.
³AkzoNobel, 6802 EM Arnhem, the Netherlands.

INTRODUCTION

The aim of this study was to increase the knowledge of the mercerisation of dissolving cellulose at low water content. This was achieved by analysing the degree of transformation of dissolving cellulose pulp to Cellulose II as a function of simultaneous variation of [NaOH]:Cellulose molar ration, [NaOH], temperature, and reaction time, by using Raman spectroscopy together with multivariate data analysis.

MATERIALS AND METHODS

A Partial least squares (PLS) regression method (Fig. 1) was applied using the average spectral mapping data of calibration set samples. The model obtained explained 99 % and predicted 99% of the variation in the degree of transformation to Cellulose II. Thus, the model obtained allowed quantification of the degree of transformation from Cellulose I in the dissolving cellulose pulp to Cellulose II.

Calibration set samples

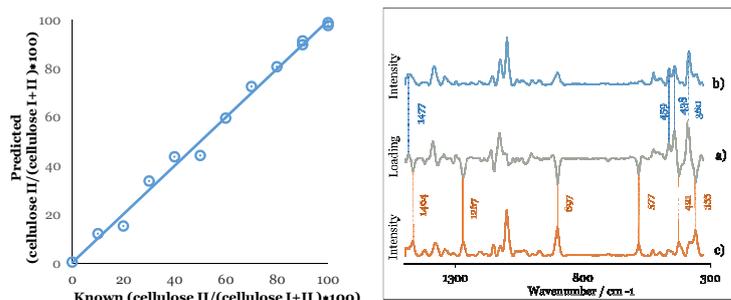


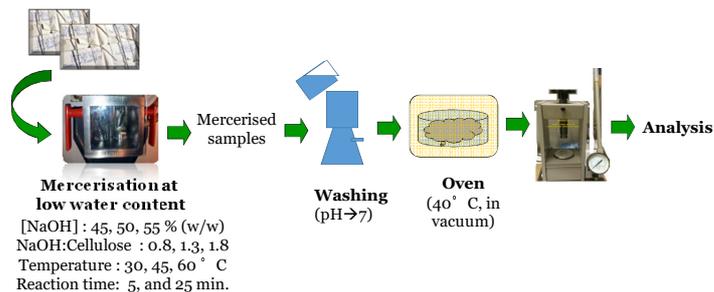
Fig. 1 Calibration model, predicted cellulose II/(cellulose I+II) as a function of known cellulose II/(cellulose I+II) for the calibration set. Calibration set samples (dots) and model line (line).

Fig. 2 a) (centre) Loading line plot for the first component of the PLS model for the Raman spectra after baseline correction and normalization for b) (top) Cell I and c) (bottom) Cell II. [2]

Samples preparation

Activation of dissolving cellulose pulp at low water content

Dissolving cellulose pulp¹



1. Dissolving cellulose pulp From DOMSJÖ Fabriker was ground to 0.28 mm mesh size.

The degree of transformation in the mercerised samples were predicted using the calibration model described above.

RESULTS AND DISCUSSION

Previous studies have indicated that temperature was important for the degree of transformation [1][3]. At the conditions in the present study, however, only the NaOH:cellulose molar ratio is very important, while temperature is not. That the [NaOH] co-varied negatively with the degree of transformation was probably due to water shortage at high concentrations. No co-variance between time and degree of transformation was observed, since the reaction occurs quickly.

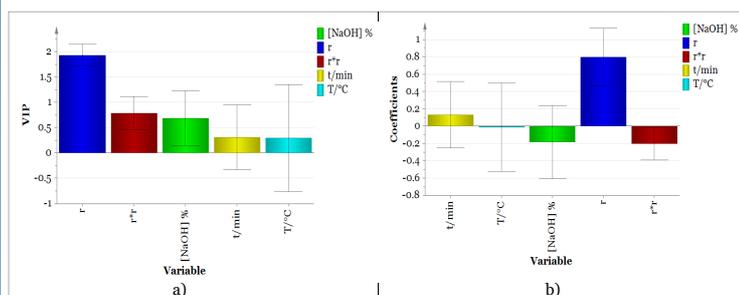


Fig. 3. a) Variable importance for the projection -VIP and b) coefficient plot showing interaction effects for degree of transformation of mercerised samples. Terms: [NaOH] = NaOH concentration in (w/w) %, (r) = NaOH: cellulose molar ratio, and (r*r) = expanded molar ratio term.

In the model increased NaOH: Cellulose molar ratio had positive influence on mercerisation. Decreased [NaOH] (a) and prolonged reaction time (b) seemed to provide higher degree of transformation to Cellulose II.

Degree of transformation to Cellulose II

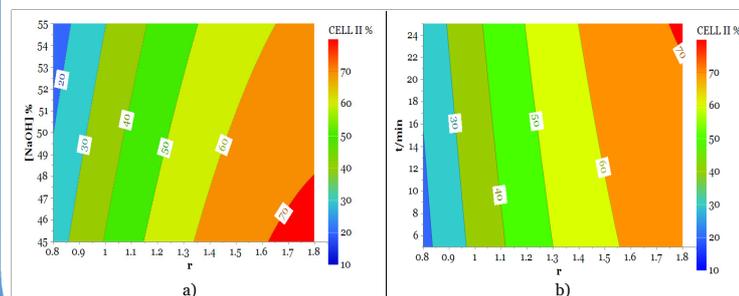


Fig 4. Contour plot for the degree of transformation to Cellulose II of mercerised samples as (a) a function of r and [NaOH] at 45 °C for 15 minutes, and (b) as a function of r and reaction time at 50 % [NaOH] and at 45 °C. Terms (r)= NaOH: Cellulose molar ratio.

Acknowledgements. Industrial Doctoral School at Umeå University, Domsjö Fabriker AB, AkzoNobel functional chemicals, Bio4Energy and The Royal Swedish Academy of Agriculture and Forestry are all acknowledged for financial support. The Vibrational Spectroscopy, and NMR platforms at KBC (UmU) are acknowledged for experimental guidance and help.

References. [1]Porro F, Bedue O, Chanzy H, Heux L (2007) Solid-state C-13 NMR study of Na-cellulose complexes. Biomacromolecules 8 (8):2586-2593.
 [2]Schenzel K, Almlof H, Germgard 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.
 [3]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.

CONCLUSIONS

In this study, Cellulose I was never completely transformed into Cellulose II. Hence neither the formation of Na-Cellulose was full. The most important factor for increasing the degree of transformation to Cellulose II was the [NaOH]:Cellulose molar ratio. Reaction time, [NaOH] and temperature did not seem to be important.