

SULPHUR-FREE COOKING FOR VALUE ADDED CELLULOSE

KATARINA KARLSTRÖM, BIRGER SJÖGREN, WALTRAUD VORWERG* and
BERT VOLKERT*

Innventia AB, Box 5604, SE-114 86 Stockholm, Sweden

**Fraunhofer Institute for Applied Polymer Research IAP, Geiselbergstrasse 69,
D-14476 Potsdam, Germany*

✉ *Corresponding author: Katarina Karlström, katarina.karlstrom@innventia.com*

To study sulphur- and chlorine-free processes to produce pulps for triacetylation and preparation of films for LCD screen application was one of the aims in the EU project AFORE. It was shown possible to produce pulp suitable for triacetylation from *Eucalyptus globulus* chips with pre-hydrolysis soda cooking and a single oxygen delignification step. Pre-hydrolysis with water at elevated temperatures extracts wood components, mainly hemicelluloses and the wood matrix is opened to facilitate alkaline pulping. After a severe pre-hydrolysis extracting some 25% of the wood raw material, a subsequent soda cook reduces the lignin content to about 1%. The oxygen delignification step produces a pulp with low lignin content, kappa no 1.4, and low hemicelluloses content, < 2 wt% xylose. The resulting cellulose had high molar mass and produced highly transparent triacetate solutions. It was also possible to produce a transparent cellulose triacetate film by solution casting with good physical properties without using plasticizer. The process also results in a sulphur-free black-liquor suitable for lignin separation by the LignoBoost process. The resulting lignin is of high purity with low hemicelluloses content.

Keywords: sulphur-free, pre-hydrolysis, soda pulping, *Eucalyptus globulus*, cellulose, CTA

INTRODUCTION

Cellulose triacetate (CTA) represents a class of cellulose derivatives used in a wide range of industrial applications, as for example manufacture of amorphous films, photographic film base and releases films in various industries.

Due to the film properties of CTA, these materials find wide applications when desired mechanical properties are reached, especially when desired optical properties are obtained. For preparing films by solution casting and evaluating the CTA film properties, a precondition is that the triacetate should be completely soluble in organic solvents.

Today, the industry is producing these films predominantly from a limited supply of cotton linters pulp. Therefore, the question whether it is possible to replace cotton with wood pulp for these applications has been raised within the AFORE¹ project.

One of the desired properties of pulps for subsequent triacetylation is limiting viscosity² in the range of 550-750 mL g⁻¹.

EXPERIMENTAL

Wood resource

Industrial *Eucalyptus globulus* wood chips were screened at Innventia over a Rader thickness screen.

The 2-8 mm fraction was selected, air-dried and hand sorted to remove chips with bark and knots.

Chips were ground, acetone extracted according to SCAN CM 49:03 and characterised with respect to their chemical composition (TAPPI T249). Quantification of carbohydrates, acid-insoluble lignin, acid-soluble lignin and ash-content was performed by using ion-chromatography, TAPPI T222 om-00, UV-spectrophotometry at 205 nm with an absorptivity coefficient of 113 L g⁻¹ cm⁻¹ and ISO 1762, respectively. Elements were determined by using ICP-AES. From analytical data, xylan, glucomannan and cellulose contents expressed as % on wood were calculated with constants for birch³ (Table 1). The elemental composition is shown in Table 2.

Fractionation of wood

Wood chips were fractionated by pre-hydrolysis with water at elevated temperatures (autohydrolysis) to remove hemicelluloses, soda cooking to delignify the wood and oxygen delignification to further remove lignin, resulting in an entirely sulphur- and chlorine-free process for production of high molar mass cellulose. The aim was to produce a cellulose pulp suitable for triacetylation. The steps followed are described below.

Pre-hydrolysis

Wood chips, 250 g as bone-dry (b.d.) weight, were charged in steel autoclaves (2.5 L). After 30 min

evacuation using vacuum, water was charged at a liquor-to-wood ratio of 6:1. The temperature was increased by 3 °C min⁻¹ to the final treatment temperature after equalization and impregnation. After 60 minutes at 150 °C or 170 °C, the autoclaves were removed from the glycol bath and cooled in water followed by removal of the free liquid by drainage.

Soda cooking +/- Anthraquinone (AQ)

Cooking liquor using 0.1 mol L⁻¹ Na₂CO₃ and 21% effective alkali (E.A.) was charged at liquor-to-wood ratio 6:1, giving [OH⁻] = 0.875 mol L⁻¹. The cook was performed at 170 °C for 150 minutes based on reference cooks without pre-hydrolysis, which produced defibrable pulp at similar residual alkali level, above 5 g L⁻¹ (0.125 g L⁻¹) for both soda and

soda-AQ processes. In the soda AQ cooks, 0.15% AQ on wood was charged (0.25 g L⁻¹).

Pulp handling

The washed delignified chips were screened in a water-jet defibrator with 1 mm perforations followed by a Wennberg screen with 0.15 mm slots. After screening, the pulps were dewatered to 25-30% consistency in a centrifuge and granulated. The unbleached screened yield and screen reject were determined gravimetrically.

Table 1
Chemical composition of wood raw material, *E. globulus*, wt% on wood

Wood component	<i>Eucalyptus globulus</i>
Klason lignin	21.5
Acid soluble lignin	4.8
Extractives (acetone)	1.1
Ash content	0.3
Xylan	17.8
(Galacto) glucomannan	3.5
Cellulose	51.0

Table 2
Elemental composition of wood raw material, *E. globulus* in mg/kg dry solids

Element	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Si
mg kg ⁻¹	4.7	4.9	732	1.8	21.4	615	775	51	102	7.3

Oxygen delignification

Oxygen delignification was carried out in teflonized autoclaves heated in a glycol-bath at 110 °C for 120 minutes with application of 0.7 MPa O₂-pressure. The alkali charge was 3% NaOH, corresponding to 30 kg ton⁻¹ pulp. The pH was measured on the filtrate. The pulp was subsequently washed in three steps with deionized water with 25 mL g⁻¹ (b. d.) pulp, twice with water at 60 °C and once at room temperature.

Pulp characterisation

The kappa number was determined according to ISO 302, limiting viscosity of the pulp in CED-solution according to ISO 5351. ISO-Brightness was determined according to ISO 3688:99 and SS-ISO 2470:2009. The monosaccharides were quantified using enzymatic hydrolysis and capillary electrophoresis.⁴

Pulp samples are designated according to pre-hydrolysis (PH) temperature in °C (X) and cooking method. Pre-hydrolysis 170 °C Soda is designated

PH170 and Pre-hydrolysis 150 °C Soda-AQ is designated PH150AQ.

Molar mass distribution (MWD) of the pulp

Pulp samples were converted to a cellulose tricarbanilate by heterogeneous synthesis with phenyl isocyanate according the following preparation steps:⁵

- defibration of freeze-dried pulp sample
- swelling in pyridine for 120 min
- reaction with phenyl isocyanate at 90 °C for 18 h
- filtration through 5 µm PTFE membrane
- precipitation with a solvent mixture of methanol, water and acetic acid
- washing with methanol/water
- drying under vacuum

For the molar mass characterization, the sample was dissolved in THF at a concentration of about 0.3 w/w%. Before the measurement with SEC-MALLS was carried out, the diluted solution was filtered through 1.0 µm PTFE membrane.

Suppliers and equipment used for SEC-MALLS

Waters; HPLC-Pump 515, Auto sampler 717 plus, Column oven, Dual Absorbance Detector 2487 and Refractive Index Detector 2414, Wyatt Technology; Laser Photometer DAWN DSP-F, 488 nm.

Triacetylation

The synthesis method with acetic anhydride as reagent and sulphuric acid as catalyst was preferred due to the applicability in the chemical industry.⁶ The formula in Figure 1 shows the desired structure.

To carry out the synthesis, freeze-dried pulps were mixed with 20 mole eq. acetic acid, 9 mole eq. acetic anhydride and 0.08 mole eq. concentrated sulphuric acid based on mole eq. anhydroglucose units (AGU) of cellulose in pulp at 50 °C. After 15-120 min, the cellulose began to dissolve in the reaction mixture. After an additional 15 min, the reaction was completed. By carefully adding acetic acid, 80 wt%, the excess of acetic anhydride, which easily reacts with

water to form acetic acid, was stabilised. After cooling of the synthesis solution, cellulose acetate was precipitated by slowly adding water. The product was washed with water and dried at 105 °C.

Determination of substitution degree of acetyl groups

The amount of acetyl groups was determined by a method based on saponification of cellulose triacetate followed by acid-base titration. The procedure was:

- 150-200 mg cellulose triacetate was swollen in 10 mL of an acetone/water mixture (1:1 by volume) for 24 h at room temperature,
- addition of 5 mL of 1 M KOH in ethanol,
- the mixture was further stirred for 24 h at room temperature,
- the excess of alkali was titrated with 0.5 M aqueous HCl by potentiometric titration.

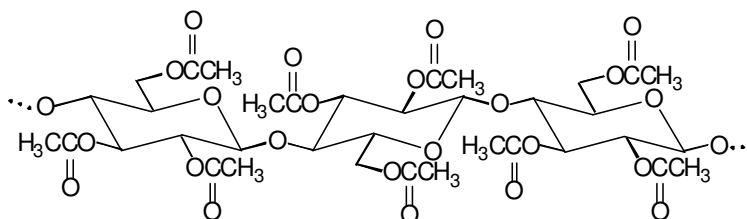


Figure 1: Triacetylated cellulose

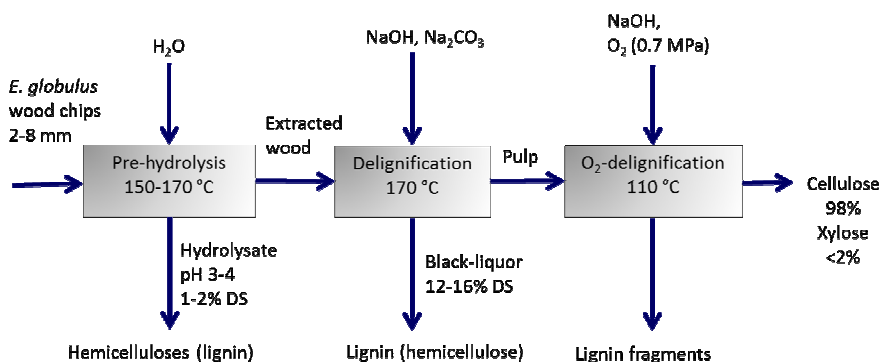


Figure 2: Outline of the developed sulphur- and chlorine free process producing pulp suitable for triacetylation

Film preparation and determination of mechanical properties

The solution of the samples in solvent methylene dichloride/methanol was prepared with a concentration of 10% (w/w). It was compared with film preparation with 30% of the plasticizer glycerine triacetate, related to CTA portion. The homogeneous and transparent solution was casted on a 100 x 20 mm PTFE-coated

glass plate and spread with a 1 mm squeegee. Afterwards, the films were dried with air and vacuum. Tensile tests of films were performed using a Zwick 1445 universal testing machine. The casted film was cut into 100 x 10 mm test pieces and evaluated in the spreading direction. The samples were conditioned at 23 °C and 50% relative humidity for 24 h before each testing.

The testing procedure was performed according to DIN EN ISO 527 and the speed used during the tensile testing was 20 mm min⁻¹. All presented data are an average of 5 tensile tests.

RESULTS AND DISCUSSION

Eucalyptus globulus dissolving pulps were produced with a sulphur- and chlorine-free process in three steps, pre-hydrolysis, soda cooking and oxygen delignification. The outline of the process using *E. globulus* is visualized in Figure 2.

Pulp composition and molecular properties

The pulps were easily defibrated in both cases and the screen reject was 0.1% on pulp. Both pulp

types had low kappa numbers after oxygen delignification (Table 3) and reached the desired limiting viscosity² for subsequent triacetylation.

The differences between the two pulp types are the degree of pre-hydrolysis and the addition of AQ. The pulp with the highest amount of cellulose, low hemicellulose content (2% xylose on pulp) and hexenuronic acid content below 0.1% (Table 4) was produced with pre-hydrolysis at 170 °C, extracting 25% of the wood raw material, followed by a pure soda cook (PH170). When a scheme with less effective pre-hydrolysis was combined with a soda-AQ cook (PH150AQ), the yield on wood was 10% higher than for PH170.

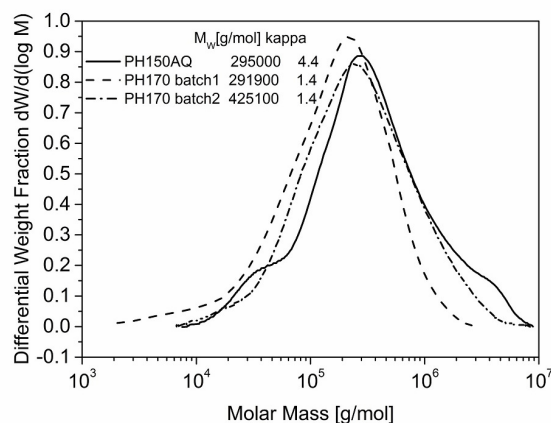


Figure 3: Molar mass distributions of *Eucalyptus globulus* wood pulps produced with pre-hydrolysis soda cooking and oxygen delignification

Table 3

Pulp characteristics for oxygen delignified pre-hydrolysis soda pulps

Pulp characteristics	PH150AQ	PH170
Kappa number	4.4	1.4
Viscosity (mL g ⁻¹)	740	630
ISO-Brightness (%)	76	81
Total yield (wt% on wood)	48	38

The molar mass distributions (MWD) of oxygen delignified pre-hydrolysis soda pulps are compared in Figure 3. The pulp sample PH150AQ showed a larger high molar mass fraction in the range of 10⁶-10⁷ g mol⁻¹ and also at 10⁸ g mol⁻¹. Swollen particles were also obtained in the THF solution of the cellulose tricarbaniolate. The tailing in the range of 10⁴-10⁶ g mol⁻¹ indicates a considerable portion of xylan, which is confirmed by the data in Table 4. The tailing was not observed at the MWD of the two separate

PH170 batches. Significant differences in MWD were shown in the molecular size of the evaluated batches of PH170, where batch 1 is lower in molar mass than batch 2.

Triacetylation and film properties

Three portions of PH170 batch 2 were triacetylated. The results are shown in Table 5. The desired high degrees of substitution in the range D.S > 2.7 with good reproducibility of the synthesis method were achieved.

The results from the mechanical testing of the produced films from PH170 batch 2 are summarized in Table 6. The values of tensile strength and Young's modulus are within a range

that guarantees good stability in usage of the films. The elongation of the film without plasticiser is above 5%, which gives sufficient flexibility of the film.

Table 4
Relative monosaccharide composition of pre-hydrolysis soda pulps
(arabinose, galactose, 4-OMe and GlcA were below detection limit, 0.1%, in both pulps)

Monosaccharide	PH150AQ	PH170
Glucose	87.2	98.5
Xylose	11.9	1.7
Mannose	0.6	<0.1
HexA	0.3	<0.1

Table 5
Results on D.S. and solubility in CH₂Cl₂/MeOH (v/v 90/10) of three separate syntheses of pre-hydrolysis soda pulp, PH170 batch 2

Synthesis	Quantity (g)	D.S.	Solubility
1	284	2.91	highly transparent
2	288	2.74	highly transparent
3	287	2.81	highly transparent

Table 6
Effect of plasticiser on mechanical strength properties of cellulose triacetate films from oxygen delignified pre-hydrolysis soda, PH170 batch 2

Films	Thickness (mm)	Tensile strength δ_{\max} (MPa)	Elongation ϵ_{\max} (%)	Young's Modulus (MPa)
- plasticiser	0.16	61.9	6.16	2012
+ plasticiser	0.20	38.1	7.81	1518

CONCLUSION

Alternative wood fractionation methods, which are sulphur- and chlorine-free, have been developed to obtain delignified and high molar mass cellulose with higher purity than that produced by current industrial processes.

The procedure involves pre-hydrolysis soda cooking and oxygen delignification and has a potential to produce dissolving pulp in an entirely sulphur- and chlorine-free process in only three steps. Using higher pre-hydrolysis temperature to remove hemicelluloses and delignification without adding anthraquinone in the soda cook, the process resulted in a pulp >98% cellulose content and was found possible to triacetylate after a single oxygen delignification step. The triacetylated cellulose produced a highly transparent solution and films with good mechanical properties without using plasticiser.

The demonstrated advantages of the combination of the proposed separation method for pure cellulose fibres with triacetylation at lab scale should be verified at industrial scale.

ACKNOWLEDGEMENTS: CELBI is acknowledged for delivery of chips. Ida Kulander and Mikaela Kubat, Innventia, are greatly acknowledged for their skilled preparation of pulps. The research leading to these results has received funding from the European Community's Seventh Framework Programme FP7/2007-2013 under grant agreement no CP-IP 228589-2.

REFERENCES

¹ AFORE (2009-2013) EU-project, Forest biorefineries: Added-value from chemicals and polymers by new integrated separation, fractionation

and up-grading technologies processes. Grant agreement no.: CP-IP 228589-2 AFORE.

² E. Sjöström, "Wood Chemistry, Fundamentals and Applications", 2nd ed., Academic Press, San Diego, CA, 1993, p. 212.

³ J. Jansson, *Faserforsch. Textiltech.*, **25** (Heft 9), 3752 (1974).

⁴ O. Dahlman, A. Jacobs, A. Liljenberg, A. I. Olsson, *J. Chromatogr. A*, **891**, 157 (2000).

⁵ U. Drechsler, S. Radosta, W. Vorwerg, *Macromol. Chem. Phys.*, **201**, 2023 (2000).

⁶ H. Steinmeier, *Macromol. Symp.*, **208**, 49 (2004).