Effect of Oligosaccharide Accumulated in the Coagulation Bath on the Lyocell Fiber Process During Industrial Production

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ABSTRACT: In this article, we investigate the effects of oligosaccharide accumulated in the coagulation bath on the lyocell fiber process during industrial production. The research method consists of three parts. First, high-performance liquid chromatography is used to analyze the monosaccharide composition of lyocell fibers and their pulp materials to determine whether the hemicelluloses in pulp material can be precipitated from the coagulation bath and then regenerated into lyocell fibers. Second, we establish a method for measuring the total sugar mixture content in the coagulation bath, which is a necessary technique during the industrial production of lyocell fibers. Third, we study the effect of oligosaccharide accumulated in the coagulation bath on the mechanical properties and supermolecular structure of lyocell fibers through a simulation experiment. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 150–156, 2009

Key words: fibers; high performance liquid chromatography (HPLC)

INTRODUCTION

Lyocell fiber[1] is a type of cellulose fiber regenerated via the *N*-methylmorpholine-*N*-oxide (NMMO) route. First, cellulose is directly dissolved in NMMO monohydrate to form a spinning solution. Second, the spinning solution is ejected through a spinneret, cooled and drawn in an air gap, immersed in a coagulation bath, and then precipitated from the coagulation bath to form a filament. The filament is washed with water and finally dried in air. Compared to the previously conventional viscose fiber route, NMMO technology provides a relatively simple, resource-preserving, and environmentally friendly method for producing regenerated cellulose fiber.

Up to now, lyocell technology has still followed the conventional viscose process, which uses pulp with a low hemicellulose content as the raw material.[2–4] This guarantees a high fiber yield in the conventional viscose process. However, the production of this pulp material carries a higher cost.

In the pulp industry, it would be less expensive to produce pulp with a high hemicellulose content. Therefore, in our research, a cheap pulp with a high hemicellulose content was used to produce lyocell fibers. This would reduce the cost of lyocell fibers to some degree.

Our previous laboratory research has shown that hemicelluloses have a generally positive influence on the quality of lyocell fiber.[5] In the laboratory, lyocell fiber preparation is not a closed-cycle process. For every process, the solvent is new. However, during industrial production, there might be hidden problems if the ejected spinning solution is not fully precipitated from the coagulation bath and then regenerated into lyocell fiber. In this case, certain low-molecular-weight hemicelluloses can dissolve and then accumulate in the coagulation bath while the lyocell fiber is continuously spun because lyocell technology is a closed-cycle process.

The aforementioned phenomenon can affect fiber formation, the properties of the obtained fiber, and solvent recovery during industrial production. Therefore, in this article, we investigate the effect of oligosaccharide accumulated in the coagulation bath on the lyocell fiber process during industrial production.

The research method includes three parts. First, the monosaccharide composition of lyocell fibers

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and their pulp materials is analyzed with high-performance liquid chromatography (HPLC) to determine whether the hemicelluloses in pulp material can be precipitated from the coagulation bath and then regenerated into lyocell fibers. Second, we establish a method of measuring the total sugar mixture content in the coagulation bath, which is a necessary technique for the industrial production of lyocell fibers. Third, we examine the effect of oligosaccharide accumulated in the coagulation bath on the mechanical properties and supermolecular structure of the obtained lyocell fibers through a simulation experiment.

EXPERIMENTAL

Analysis of the monosaccharide composition of the lyocell fibers and their pulp materials

Materials and reagents

Pulp 1 (a cheap pulp with a high hemicellulose content) was supplied by Weyerhaeuser (Covington, WA). Pulp 2 (a conventional pulp with a low hemicellulose content) was purchased from Sappi Saiccor (Durban, South Africa). Their degrees of polymerization (measured by the cuprammonium hydroxide solution method) were 547 and 633, respectively. Lyocell fiber 1 was produced from pulp 1. Lyocell fiber 2 was produced from pulp 2.

Sugar standards were obtained from Sigma (Milwaukee, WI). They included D-mannose (Man), D-glucose (Glu), D-galactose (Gal), and D-xylose (Xyl). 1-Pheny-3-methyl-5-pyrazolone (PMP), a UV derivative reagent, was purchased from Acros (Trenton, NJ). Acetonitrile and methanol were HPLC-grade and were obtained from DaHu Science Co., Ltd. (Shanghai, China). Butyl ether (analytical purity) was purchased from LinFeng Chemical Co., Ltd. (Shanghai, China). Sodium dihydrogen phosphate and disodium hydrogen phosphate (analytical purity) were obtained from China National Medicines Co., Ltd. (Shanghai, China). Milli-Q water was used in the experiments.

Sample pretreatment

D-Man, D-Glu, D-Gal, and D-Xyl were used for standard sugar solution preparation. Each monosaccharide was dissolved in methanol to a concentration of 10 mg/mL in an Eppendorf tube. Ten milliliters was then extracted from each tube and mixed in another Eppendorf tube.

Test samples were pulp 1, pulp 2, fiber 1, and fiber 2. The polymers of fiber or pulp sugars were converted into monomers by sulfuric acid digestion as follows.[6–8]

The fibers and pulps were ground and dried at 50°C *in vacuo*. The sample size for each analysis was 400 mg. The sample was hydrolyzed for 1 h at 30°C in 72% (w/w) H_2SO_4. The sulfuric acid solution was then diluted to a concentration of 3% (w/w), and the mixture was hydrolyzed continuously for 1 h at 120°C. The solution was filtered and neutralized to pH 7 with barium hydroxide. The barium sulfate precipitate was allowed to settle overnight in the refrigerator and was filtered the next day. Each sample was concentrated to 10 mL and filtered with a 0.45-μm membrane. Fifty microliters was then extracted from each hydrolysate solution and placed in an Eppendorf tube.

PMP derivatization

The prepared standard solution and sample solution were brought to dryness and reacted through the addition of 40 μL of 0.3*M* NaOH and 40 μL of a 0.5*M* PMP solution in methanol. The mixtures were heated at 70°C for 30 min and then neutralized with 40 μL of 0.3*M* hydrochloric acid. Butyl ether (1 mL) was added. The organic phase was discarded after shaking. This extraction process was repeated three times. The water phase was diluted to 1 mL, filtered with a 0.45-μm membrane, and analyzed by HPLC.[9–13]

HPLC analysis

HPLC analysis was performed with the Waters Breeze system (Waters, Milford, MA) equipped with a constant-flow pump (Waters 1525) and a biwave UV detector (Waters UV4810). The column was Hypersil ODS2 (5 μm, 150 mm × 4.6 mm), and it was preceded by a guard column.

Elution was performed at 1 mL/min with solvents A and B. Solvent A was 50 mmol of a phosphate buffer solution with pH adjustment (pH ~ 6), and solvent B was acetonitrile. The mixture was A–B (77/23 v/v). The system was controlled at room temperature. The detection was performed at 245 nm. The injection volume was 20 μL, and the running time was 10 min.

Measurement of the total sugar mixture content in the coagulation bath

Measurement method

Back-titration was employed to measure the total sugar mixture content in the coagulation bath. Here the sugar mixture included a six-carbon saccharide (D-Glu, D-Gal, and D-Xyl) and a five-carbon saccharide (D-Man). Meanwhile, the percentage of each saccharide in the sugar mixture was equal to the monosaccharide composition of lyocell fiber 1.

At first, the full oxidation of the sugars with potassium dichromate ($K_2Cr_2O_7$) was based on eqs. (1) and (2):

$$C_6H_{12}O_6 + 4Cr_2O_7^{2-} + 32H^+ = 8Cr^{3+} + 6CO_2 + 22H_2O \quad (1)$$

$$3C_5H_{10}O_5 + 10Cr_2O_7^{2-} + 80H^+ = 20Cr^{3+} + 15CO_2 + 55H_2O \quad (2)$$

$K_2Cr_2O_7$ (which does not react to sugars) was titrated back with ammonium ferrous sulfate [$(NH_4)_2Fe(SO_4)_2$] according to eq. (3):

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (3)$$

At the end point of the reaction, with a ferroin indicator, the solution color changed from olive green to red.

Calculation formula

On the basis of eqs. (1)–(3) and the percentage of each saccharide in the sugar mixture, the calculation formula of the total sugar mixture content in the NMMO aqueous solution is educed:

$$\text{Sugar}\% = \frac{(V_{\text{blank}} - V_{\text{unknown}}) \times 10^{-3}}{m_{\text{sample}}} \times C_{\text{titrating}} \times 7.5 \times 100 \quad (4)$$

where m_{sample} (mg) is the mass of the blank solution or unknown solution and the masses of the two solutions are equal. V_{blank} is the consumed volume of $(NH_4)_2Fe(SO_4)_2$ in the titration of the blank solution with a standard $K_2Cr_2O_7$ solution. The blank solution is the coagulation bath, which is 9% (w/w) NMMO in distilled water. V_{unknown} is the consumed volume of $(NH_4)_2Fe(SO_4)_2$ in the titration of the unknown solution with a standard $K_2Cr_2O_7$ solution. The unknown solution is the blank solution with the dissolved sugar mixture, that is, D-Man, D-Glu, D-Gal, and D-Xyl, according to the previously analyzed monosaccharide composition of lyocell fiber 1. $C_{\text{titrating}}$ (mol/L) is the concentration of the standard $(NH_4)_2Fe(SO_4)_2$ solution and is calculated as follows:

$$C_{\text{titrating}} = \frac{0.200 \times 10 \times 6}{V} \quad (5)$$

where V is the consumed volume of $(NH_4)_2Fe(SO_4)_2$ in the titration of $(NH_4)_2Fe(SO_4)_2$ with a standard $K_2Cr_2O_7$ solution.

Here, all titration volumes (mL) came from more than three measurements. The standard $K_2Cr_2O_7$ solution (0.200 mol/L), the ferroin indicator, and the standard $(NH_4)_2Fe(SO_4)_2$ solution were all laboratory-produced.[14,15]

Effect of oligosaccharide accumulated in the coagulation bath on the lyocell fiber process

Lyocell fibers regenerated from the coagulation bath with different sugar mixture contents

A spinning solution with a 12% (w/w) concentration of pulp 1 in NMMO·H_2O was extruded through a spinneret with 100 orifices (80 μm in diameter) with a gear pump. The ejected spinning solution was cooled and drawn (100 m/min) in an air gap and then immersed in a coagulation bath (15°C) to form filaments. The filaments were washed with water and finally dried in air.

Here the coagulation bath was 9% (w/w) NMMO in distilled water with different sugar mixture contents, such as 0, 5, 10, and 15%, until a saturation status was reached. The lyocell fibers regenerated from the coagulation bath with different sugar mixture contents were characterized as follows.

Mechanical property measurement

The mechanical properties of the lyocell fibers were measured with an XQ-1 tensile tester (China Textile University, Shanghai, China). The sample length was 20 mm, and the extension rate was set at 4 mm/min. The results came from more than 25 measurements of each specimen. All measurements were performed at 20°C and 65% relative humidity.

Wide-angle X-ray diffraction study

Wide-angle X-ray diffraction was performed on a D/MAX-γB diffractometer (Rigaku, Tokyo, Japan; Cu Kα wavelength = 0.154 nm). The obtained data were analyzed with Peakfit software to calculate the crystallinity.

Birefringence measurements

Birefringence measurements of the lyocell fibers were performed with an Olympus XP51 optical polarized light microscope with a Berek compensator (Olympus Co., Tokyo, Japan).

Orientation factor measurement

The azimuthal intensity distribution of the equatorial reflection at 21.7° was used for determining the crystalline orientation factor (f_c):

$$f_c = 1 - \frac{W_{1/2}}{180} \quad (6)$$

where $W_{1/2}$ is the full width at the half-height of the azimuthal intensity distribution for the (002) plane.

Furthermore, the amorphous orientation factor (f_a) was calculated with the Stein equation:

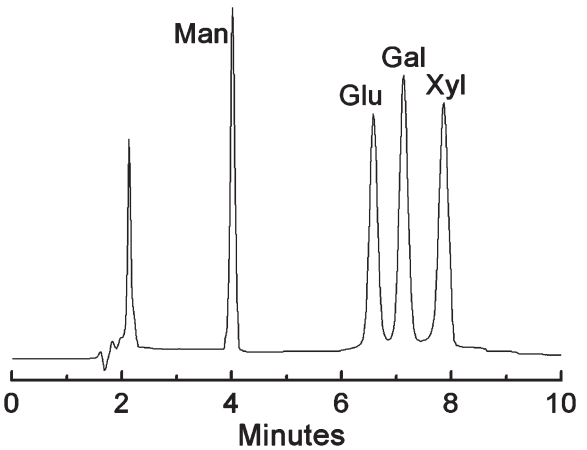

Figure 1 HPLC chromatogram of four PMP-labeled standard sugars.

$$\Delta n = \alpha f_c \Delta n_{co} + (1 - \alpha) f_a \Delta n_{ao} \quad (7)$$

where Δn is the total fiber birefringence; α is the crystallinity; and Δn_{co} and Δn_{ao} are the characteristic birefringences of the crystalline phase and the amorphous phase, respectively. Here it is assumed that $\Delta n_{co} = \Delta n_{ao} = 0.0545$.[16]

RESULTS AND DISCUSSION

Analysis of the monosaccharide composition of the lyocell fibers and their pulp materials

HPLC separation of PMP-labeled standard sugars

Figure 1 shows an HPLC chromatogram obtained after the injection of a sugar mixture solution of D-Man, D-Glu, D-Gal, and D-Xyl (166.5 ppm of each). The sugar mixture separated well. The retention time of the individual sugar was determined first, and the linear standard curve equation for each sugar (listed in Table I) was obtained according to the HPLC chromatogram of the sugar mixture solution at different concentrations, that is, 416.5, 166.5, 83.3, 55.5, and 27.5 ppm. These equations were used to calculate the monosaccharide compositions of the samples.[9–13,17]

HPLC separation of PMP-labeled hydrolysate sugars

Figures 2 and 3 show HPLC chromatograms of PMP-labeled hydrolysate sugars from the lyocell fibers and their pulp materials. Here, Glu was the hydrolysate of cellulose. Man, Gal, and Xyl were the hydrolysates of hemicelluloses. Therefore, the total composition of Man, Gal, and Xyl was the hemicellulose content. According to the linear standard curve equation of the individual sugar, the monosaccharide compositions of the lyocell fibers and their pulp materials were calculated, and they are listed in Table I.

Comparing Figure 2(a,b) and Figure 3(a,b), we can see that the HPLC chromatograms of the PMP-labeled hydrolysate sugars of the lyocell fibers and their pulp materials are almost the same. Furthermore, from Table I, it can be more clearly seen that the monosaccharide composition and the total hemicellulose content in the lyocell fibers and their pulp materials were approximately equal. Therefore, for each spinning process, it is likely that not only cellulose but also most hemicelluloses can be precipitated from the coagulation bath and then regenerated into lyocell fibers.

However, during industrial production, there might be hidden problems because a characteristic of lyocell technology is the closed-cycle process. Table I shows that the total hemicellulose content of lyocell fibers is slightly lower than that of their pulp materials. That is, some hemicelluloses are not precipitated from the coagulation bath. They dissolve in the coagulation bath and then accumulate for months while lyocell fibers are continuously spinning.

Some questions remain. How much oligosaccharide can accumulate in the coagulation bath? Does the accumulated oligosaccharide have an effect on the lyocell fiber process? We carried out simulation experiments on these problems in advance.

Measurement of the total sugar mixture content in the coagulation bath

Establishment of a method for measuring the total sugar mixture content in the coagulation bath

A long period of time is required to accumulate oligosaccharide in the coagulation bath. In our work, it was impossible to measure the total sugar mixture content in the coagulation bath, which was continuously spinning lyocell fiber for months on end. By the simulation of this phenomenon at 0°C, a sugar

TABLE I
Monosaccharide Composition and Total Hemicellulose Content in Lyocell Fibers and Their Pulp Materials

Sample	Pulp 1	Fiber 1	Pulp 2	Fiber 2	Linear equation
Glu (%)	78.99	79.18	90.18	90.32	$A = -3.65 \times 10^5 + 1.14 \times 10^4 C$
Man (%)	9.24	9.17	1.08	1.04	$A = -3.26 \times 10^5 + 1.25 \times 10^4 C$
Gal (%)	1.16	1.05	1.50	1.40	$A = -2.18 \times 10^5 + 1.15 \times 10^4 C$
Xyl (%)	10.61	10.60	7.24	7.24	$A = -3.81 \times 10^5 + 1.34 \times 10^4 C$
Hemicelluloses (%)	21.01	20.82	9.82	9.68	

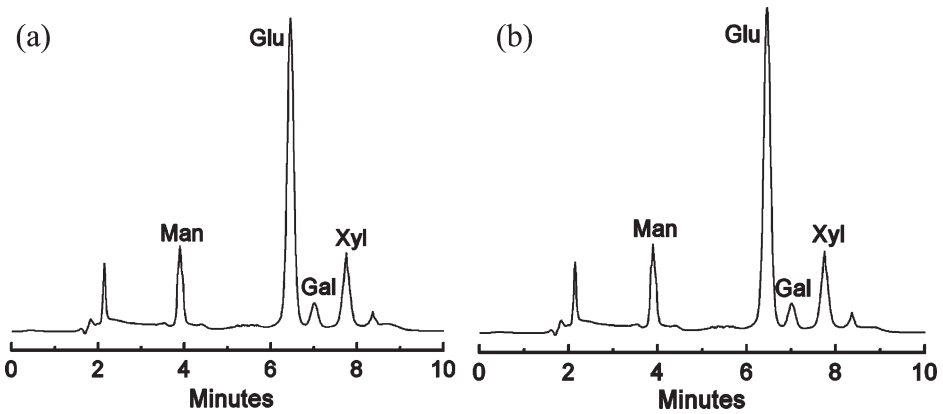

Figure 2 HPLC chromatograms of PMP-labeled hydrolysate sugars. (a) fiber 1 and (b) pulp 2.

mixture was dissolved in the coagulation bath to saturation. The total sugar mixture content was then measured via a back-titration method. The calculation formula could be educed from the redox equations and the percentage of the individual monosaccharide in the sugar mixture. The coagulation bath needs regeneration and reuse. Therefore, it is important to establish a method of measuring the total sugar mixture content in the coagulation bath. This offers a technique for detecting compositional changes of the coagulation bath.

Total sugar mixture content in the coagulation bath for spinning lyocell fiber 1

In terms of the redox equations and the percentage of the individual monosaccharide of lyocell fiber 1, the calculation formula of the total sugar mixture content in the coagulation bath has been educed and is given as eq. (4). The calculations are listed in Table II. Table II shows that the saturation value of the sugar mixture dissolved in the coagulation bath (9% w/w NMMO aqueous solution) at 0°C was about 32%. For the saturated solution, the oligosaccharide that accumulated in the coagulation bath could be precipitated and filtered by a 0.2-μ nylon membrane. However, for the unsaturated solution, it is possible that the oligosaccharide that accumulated in the coagulation bath affected the lyocell fiber process. This problem was further investigated as follows.

Effect of oligosaccharide accumulated in the coagulation bath on the lyocell fiber process

Lyocell fibers regenerated from the coagulation bath with different oligosaccharide contents

Here too a long period of time is required to accumulate the oligosaccharide in the coagulation bath. In our work, it was impossible to study the effect of oligosaccharide accumulated in the coagulation bath on the lyocell fiber process, which was continuously spinning lyocell fiber for months on end. Through the simulation of this phenomenon at 0°C, a sugar mixture was dissolved in the coagulation bath to saturation. Lyocell fibers were then produced under different sugar mixture content conditions in the coagulation bath, that is, 0, 5, and 10% and up to 30%.

During spinning under the aforementioned conditions, there were no broken or fused filament

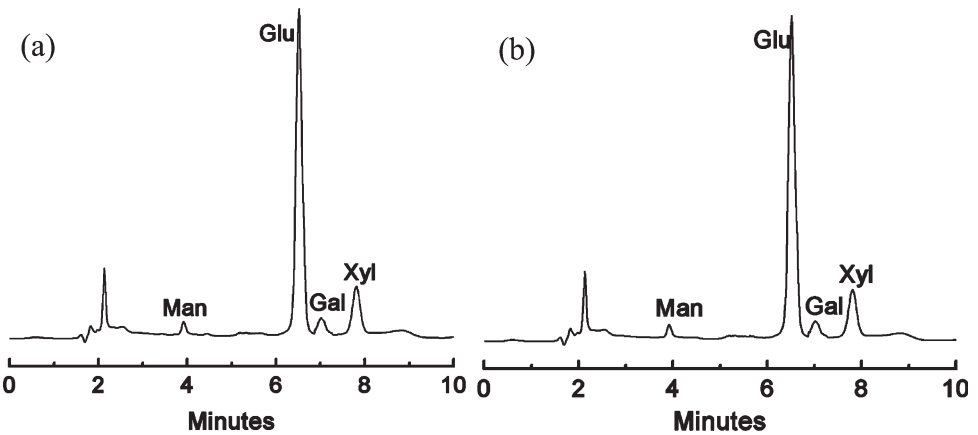

Figure 3 HPLC chromatograms of PMP-labeled hydrolysate sugars. (a) fiber 2 and (b) pulp 2.

TABLE II
Saturation Value of a Sugar Mixture Dissolved in a 9% (w/w) NMMO Aqueous Solution at 0°C

Measurement parameter	Measurement result
V (mL)	119.50
$C_{titrating}$ (moL/L)	0.1090
m_{sample} (mg)	242.9
$V_{blank} - V_{unknown}$ (mL)	95.20
Saturation value (%)	32.04

TABLE IV
Supermolecular Structure of Lyocell Fiber Regenerated from a Coagulation Bath With or Without a Sugar Mixture Dissolved in It

Sugar mixture content in the coagulation bath (%)	α (%)	f_c	f_a	Δn
0	49	0.827	0.5309	0.03685
30	48	0.827	0.5335	0.03675

phenomena, and the whole spinning system was stable. The mechanical properties and supermolecular structure of these obtained lyocell fibers were researched further.

Effect of oligosaccharide accumulated in the coagulation bath on the mechanical properties and supermolecular structure of the lyocell fibers

Table III shows the mechanical properties of lyocell fibers regenerated from the coagulation bath with different sugar mixture contents. There was no big difference in the titer, the elongation at the break, the tensile strength, or the modulus.

Table IV shows the supermolecular structure of lyocell fiber regenerated from the coagulation bath without or with the sugar mixtures dissolved in it. There was no significant difference in the crystallinity or orientation.

The data from Tables III and IV indicate that there was no significant effect of oligosaccharide accumulated in the coagulation bath on the mechanical properties and supermolecular structure of the lyocell fibers.

Theoretically,[18] the mechanism of the coagulation process of lyocell fiber is a bidirectional diffusion process. As soon as the filament (ejected spinning solution) enters the coagulation bath, NMMO in the filament diffuses into the coagulation bath, and the coagulant (water) in the coagulation bath diffuses into the filament. As a result, phase separation takes place, and cellulose is precipitated to form the filament. During this coagulation process, the velocity of bidirectional diffusion affects the structural formation and properties of the obtained fibers. The velocity of bidirectional diffusion mainly depends on the concentration of NMMO in water. The obtained experimental data also indicate that the velocity of bidirectional diffusion does not depend on the oligosaccharide content in the coagulation bath. Consequently, the oligosaccharide that has dissolved and accumulated in the coagulation bath does not significantly affect the fiber formation or the properties of the obtained fibers.

TABLE III
Mechanical Properties of Lyocell Fibers Regenerated from a Coagulation Bath with Different Sugar Mixture Contents

Sugar mixture content (%)	Titer (dtex)	Elongation at break (%)	Tensile strength (cN/dtex)	Modulus (cN/dtex)
0	2.20	8.5	3.96	39.4
5	2.23	8.6	3.93	39.5
10	2.25	9.1	3.47	36.7
15	2.25	9.3	3.71	40.1
20	2.23	9.0	3.62	38.5
25	2.24	9.0	3.70	38.1
30	2.26	8.6	3.80	41.6

CONCLUSIONS

The monosaccharide composition of the lyocell fibers and their pulp materials was approximately equal. It was proved that not only cellulose but also hemicelluloses could precipitate from the coagulation bath and then regenerate into the lyocell fiber for each spinning process. However, during closed-cycle industrial production, it is possible that some oligosaccharide can dissolve and accumulate in the coagulation bath when the lyocell fiber is continuously spinning for months on end.

A method of measuring the total sugar mixture content in the coagulation bath was established. This is a necessary technique for detecting the compositional changes of the coagulation bath during the industrial production of lyocell fiber because the coagulation bath needs regeneration and reuse. For the production of lyocell fiber 1 from pulp 1, it was determined that the saturation value of the sugar mixture accumulated in the coagulation bath (9% w/w NMMO aqueous solution) at 0°C was about 32%.

In the industrial production of lyocell fiber, some oligosaccharide will dissolve and accumulate in the coagulation bath, but this phenomenon does not significantly affect the lyocell fiber process. However, it is possible that this phenomenon will affect solvent recovery. Therefore, in the future, further work will be carried out to study the effect of oligosaccharide

accumulated in the coagulation bath on solvent recovery during the lyocell fiber process.

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