Hydrotropic Fractionation of Birch Wood into Cellulose and Lignin: A New Step Towards Green Biorefinery

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Hydrotropic treatment is an attractive process that uses water-soluble and environmentally friendly chemicals. Currently, this method is practically unexploited on a large scale due to the long treatment times required. In this study, the hydrotropic process was modified by the addition of hydrogen peroxide, formic acid, or both. The modified treatments were more selective than the reference, and the pulps obtained using the modified treatments had lower lignin contents. After bleaching, the resultant pulps were comparable to dissolving pulps with respect to the content of hemicelluloses and viscosity. Cellulose solutions were successfully obtained in a 7% NaOH/12% urea aqueous solvent after pretreating the bleached pulp with a HCl/EtOH mixture. Hydrotropic lignin was recovered from the spent solution by precipitation in water. The lignin had very low contents of carbohydrates and sulphur. The preliminary results show that a hydrotropic process can be used for such biorefinery applications as fractionation of fibres, cellulose polymer, and lignin from birch wood. The green cellulose and lignin biopolymers can potentially be used for shaping biomaterials or production of bio-based chemicals.

Keywords: Hydrotropic treatment; Sodium xylenesulphonate; Birch wood; Hydrotropic lignin; Hydrotropic pulp

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INTRODUCTION

Hydrotropic agents are water-soluble organic substances that have both hydrophilic and hydrophobic functionalities in their chemical structure and, at concentrations high enough to form molecular aggregates, are capable of improving the aqueous solubility of water-insoluble organic substances (Balasubramanian and Friberg 1993). Although hydrotropic agents resemble surfactants in some ways, these two classes of compound are distinct from each other with respect to the hydrophobic chain, which is usually shorter in the case of hydrotropes. This distinction in the size of the hydrophobic chain governs other practical differences. Specifically, a relatively high concentration of a hydrotrope in the solution is required for solubilisation of a solubilisate, and the amount of the compound being solubilised by hydrotropic solutions is much higher than that by solutions of surfactants (Balasubramanian and Friberg 1993).

The application of hydrotropes for biomass processing was initiated by McKee (1943), who patented the pulping of different lignocellulosic raw materials with concentrated solutions of benzene-derived hydrotropic salts. As an example, McKee describes the hydrotropic pulping of poplar wood with a 30% solution of sodium xylenesulphonate. The cooking was carried out for 12 h at a temperature of 150 °C. According to the patent and another publication of McKee (1954), hydrotropic treatments have several advantages over commercial pulping processes. The process is environmentally friendly, with low consumption of the cooking agent. It is also possible to recover large quantities of lignin in combination with by-products such as carbon dioxide and furfural. The spent solution from the first cooking can be reused 5 to 6 times until it becomes saturated with dissolved lignin (about 350 g/L); this saves energy for heating the cooking solution before pulping. The recovery process of the cooking solution is simple, and it is comprised of three steps: dilution of the spent solution with water, filtration of the precipitated lignin, and evaporation of the diluted solution until reaching the operating concentration (30 to 40%). Additional by-products are formed during hydrotropic treatment, which are acetic and formic acids (Gromov 1963; Nelson 1978), dissolved hemicelluloses, and sugar monomers (Gromov and Odincov 1957a; Jayme and Rosentstock 1958). The amounts of the latter two as well as furfural depend strongly on the cooking conditions and impurities that are present in the hydrotropic agent (Gromov and Odincov 1957a; Domburg and Gromov 1964; Jayme and Rosentstock 1958; Gromov and Khrol 1964). Most of the by-products, if recovered, could bring additional revenue to the mill.

Owing to the benefits, hydrotropic treatment has attracted great scientific interest during the 1950s through the1980s as a new cooking method that would be an alternative to the existing pulping technologies. Many studies were conducted in these years with the purpose of process optimization and improvement of the pulp properties. This was attempted by altering cooking conditions (Gromov and Odincov 1959), using different hydrotropic agents (Procter 1971), using other solvent media instead of water (Procter 1971), and modification of hydrotropic cooking solutions with various additives (Nelson 1978; Kalninsh *et al.* 1967; Treimanis *et al.* 1981). Most of the research was done with a focus on manufacturing paper-grade pulps. However, despite all the efforts, the process did not become superior to traditional sulphite and alkaline pulping methods with respect to the properties of paper-grade pulps. Hydrotropic pulp usually has lower brightness than sulphite pulps (Procter 1971) and worse mechanical properties than alkaline pulps (Nelson 1978; Procter 1971). Moreover, the yield of pulp from hydrotropic treatment was lower than of pulps produced by the conventional methods at similar lignin contents (Procter 1971; Gromov and Tupureine 1960). Although some modifications, *e.g.*, the addition of alkali, could improve mechanical properties, they led to problems associated with the recovery of the cooking solution (Procter 1971). Another significant drawback of the hydrotropic process was its unsuitability for pulping softwoods (Nelson 1978; Korpinen and Fardim 2009), which was explained by the difference in the structure of lignins from softwoods (guaiacyl type) and hardwoods (syringyl-guaiacyl type). Softwood lignin is more prone to condensation reactions in acidic media than hardwood lignin (Procter 1971).

Nevertheless, hydrotropic treatment could attract great attention as a process for biomass fractionation into lignin and cellulose (Fig. 1) because of increasing demand for bio-based materials to replace oil-based ones. Lignin recovered from the process can potentially be used as a source of phenolic substances, as a binder for composites, and as a raw material for the production of activated carbon and carbon fibres. Alternatively, it can be burned to produce heat and energy. The pulp has a high content of alpha-cellulose (McKee 1943). Generally, it can be utilized for the production of fibres, films, beads, or for the synthesis of various cellulose derivatives. Apart from lignin and cellulose, other by-products (listed in the figure) can be recovered and used for various applications or for synthesis of chemicals.

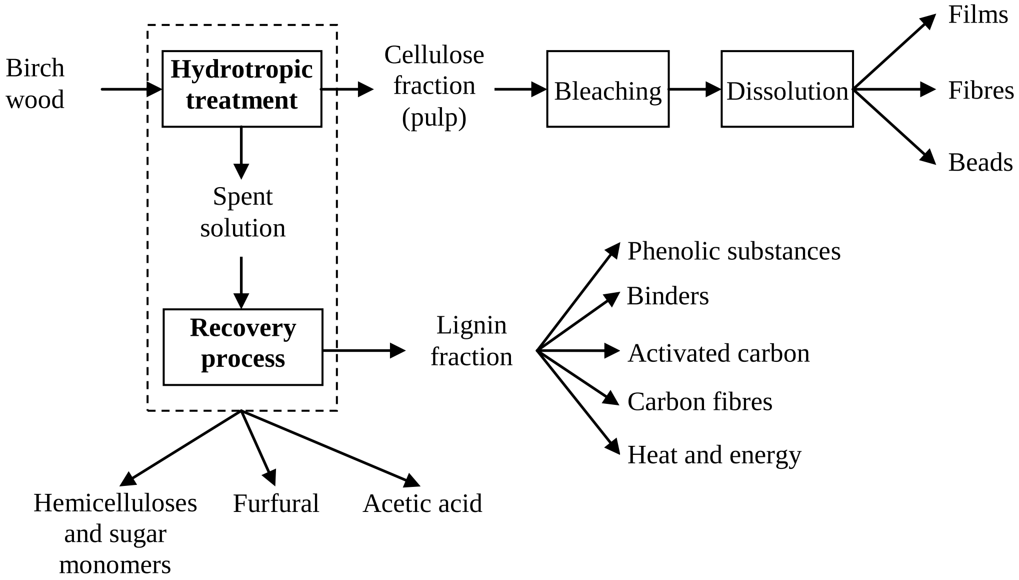

Fig. 1. Hydrotropic fractionation of birch wood

A recent study (Korpinen and Fardim 2009) showed that hydrotropic treatment of birch wood for 12 h at 150 °C removed most of the lignin and hemicelluloses present in the wood, and the lignin precipitated from the spent solution was sufficiently pure to be used as a raw material for further conversion. However, the long treatment time made the process impractical; therefore, the main objective of this research was to modify the treatment to reduce its duration and improve its performance. Additionally, this work includes bleaching and cellulose dissolution experiments. Finally, one segment is devoted to the recovery of lignin and its analysis.

EXPERIMENTAL

Materials

Birch chips collected from a Finnish pulp and paper mill were screened in a laboratory, and the fraction of thickness 4 to 6 mm was used for the experiments. The chemical composition of birch wood was (%): acetone-soluble matter 2.0, lignin 23.1, and cellulose 40.6. The non-cellulosic carbohydrates (as anhydrous units, %) were: arabinose 0.4, xylose 20.2, rhamnose 0.5, mannose 1.0, galactose 0.7, 4-*O*-Me-glucuronic acid 1.4, galacturonic acid 0.9, and glucose 1.6.

Methods

Hydrotropic treatment

All treatments were done in laboratory-scale batch digesters using a 36% aqueous solution of the hydrotropic reagent sodium xylenesulphonate (technical grade, purity >90%, Sigma-Aldrich). The solutions were modified by adding hydrogen peroxide, formic acid, or both. The additives and their dosages used in the experiments are shown in Table 1. Other conditions were selected according to the literature (Kalninsh *et al.*

1967) and trial experiments: heating rate 1.5 °C/min, dwell temperature 170 °C, dwell time 2 h, and liquor-to-wood ratio 4 w/w. Before the treatments, the chips were impregnated with the hydrotropic solutions for 30 min under vacuum. After the treatments, the chips were disintegrated. The obtained pulps were washed with tap water until the pulps stopped foaming, and then they were further washed batch-wise with a 0.5% NaOH solution for 10 min. The amount of the NaOH solution was 6 times the amount (w/w) of the wood. Then the pulps were washed again with tap water until clear filtrates were obtained and screened in a laboratory screen with a 0.06 mm slit basket.

Table 1. Designation of Hydrotropic Treatments and Dosages of Chemicals Used for Modification of Hydrotropic Treatments

Hydrotropic treatment designation	Hydrogen peroxide, % (w/w) on o.d.* wood	Formic acid, % (w/w) on o.d. wood
R (reference)	-	-
H	2.5	-
F	-	2.6 (pH 3.5)
HF	2.5	2.1 (pH 3.5)
* o.d. – oven-dry R = Reference; H = H_2O_2; F = Formic acid; HF = H & F together		

Oxygen delignification and bleaching

Two selected pulps with the highest and the lowest kappa number and viscosity values (R and HF, as denoted in Table 1) were subjected to oxygen delignification and bleaching. Conditions of the oxygen delignification stage were as follows: temperature 95 °C, time 60 min, pressure 6 to 7 bar, NaOH charge 20 kg/t o.d. pulp, and $MgSO_4$ charge 3 kg/t o.d. pulp. After oxygen delignification, the pulps were bleached with a totally chlorine free (TCF) sequence Q-PO-Q-P (Table 2). The conditions and dosages of the chemicals for the Q stage were chosen according to Anderson and Amini (1996), for the PO bleaching stage based on a work by Wackerberg *et al*. (1997), and for the P stage according to trial small batch experiments. Oxygen delignification and the PO stage were carried out in a Quantum Mark IV mixer. The other stages were performed in plastic bags placed in a thermostatic bath. After the bleaching stages, the pulps were washed with distilled water until the liquor squeezed from the pulp had a neutral pH.

Table 2. Bleaching Conditions and Dosages of Chemicals Used in Bleaching

Stages	Q	PO	Q	P
Conditions				
Temperature, °C	70	90	70	90
Time, min	60	30 (HF), 120 (R)	60	270
Consistency, %	10	10	10	10
pH	6-7	-	6-7	-
Pressure, bar	-	5	-	-
Chemicals, kg/t o.d. pulp				
DTPA*	2	-	2	-
Hydrogen peroxide	-	35	-	30
NaOH	-	30	-	30
$MgSO_4$	-	3	-	3
*DTPA – diethylenetriaminepentaacetic acid				

HCl/EtOH pretreatment and rheological measurements

HF-bleached pulp was pretreated with a HCl/EtOH mixture for 2 h at 75 °C. The pretreatment procedure and post-handling of the pretreated pulp are described in detail in the literature (Trygg and Fardim 2011). The pretreated HF pulp was used to prepare cellulose solutions of different concentrations (0, 0.2, 1, 2, 3, 4, and 5%). A 7% NaOH/12% urea aqueous solution was chosen for the dissolution as a cheap and environmentally friendly, water-based solvent (Qi *et al.* 2008; Trygg and Fardim 2011). Before dissolution, the pulp was disintegrated in solvent by stirring to destroy the flocks. The homogenised suspension was placed inside a cooler and kept there at a temperature between -10 °C and -12 °C for 30 min. The obtained solutions were examined with a microscope to verify that the solution was clear and then centrifuged at 3500 rpm for 10 min to settle non-cellulosic contaminants.

The rheological behaviour of the cellulose solutions was studied with a shear rheometer (Anton Paar Physica MCR 300) employing a double-gap cylinder. For each concentration, the measurements were performed at several temperatures (±0.01 °C): 10, 15, 20, and 25 °C. Between measurements, the solutions were stored in a cold room (6 °C), and a new sample was used for each of the temperatures. The viscosity-shear rate data obtained from the rheological measurements were used to calculate apparent activation energy of a viscous flow (E_a) as described in the literature (Roy *et al*. 2003; Trygg and Fardim 2011).

Analyses of wood and pulps

The preparation of pulps for analysis was done following the guidelines in the corresponding procedures. Prior to analysis, the wood was ground with a cutting mill using a sieve cassette with 1 mm trapezoidal perforations. The following standard analyses were performed: kappa number (SCAN-C 1:00), brightness (ISO 3688), hexenuronic acid (Chai *et al.* 2001), viscosity (ISO/FDIS 5351), and lignin content (TAPPI T222 om-02 with some modifications according to Schwanninger and Hinterstoisser (2002) and TAPPI UM 250). Prior to the determination of lignin content, the samples were extracted with an acetone-water mixture (95:5 v/v) according to SCAN-CM 49:03.

The non-cellulosic carbohydrates in the wood and pulps were analysed by acid methanolysis and gas chromatography (GC) as described in the literature (Sundberg *et al.* 1996) with some exceptions. The samples with the methanolysis reagent were kept in an oven for 5 h. After the reaction the acid was neutralized with 200 µL of pyridine, and 1 mL (4 mL for the wood samples) of a 0.1 mg/mL solution of resorcinol in methanol was added as an internal standard. The cellulose content was determined by acid hydrolysis with 72% sulphuric acid and GC according to Sundberg *et al.* (2003). Cotton linters were used as a calibration standard. The amount of cellulose was calculated, taking into account glucose that originates from glucomannan (Janson 1974).

Isolation and analysis of lignin

The precipitation procedure was done based on Korpinen and Fardim’s work (2009). Sixty mL of the spent solution from the reference treatment was diluted with 600 mL of water, stirred for 1 h, and centrifuged to separate the lignin precipitate and the liquid. The lignin was washed batch-wise twice by stirring for 1 h with 600 mL of distilled water and centrifuging. The washed lignin was freeze-dried and used for further analysis.

The sulphur content of the lignin was measured by BELAB AB (Norrköping, Sweden) according to SS-EN 15289/15408. The composition of residual carbohydrates in the lignin was analysed by acid methanolysis and GC, which was done in the same manner as described earlier (see *Analyses of wood and pulps*), except that the samples were kept in an oven for 3 h.

RESULTS AND DISCUSSION

Hydrotropic Treatment

The additives used to modify the hydrotropic process had two contrary effects, as can be observed from the data in Table 3. Addition of either hydrogen peroxide or formic acid alone resulted in a lower lignin content (kappa number) in comparison with the reference treatment. Hydrogen peroxide at the applied concentration was more efficient as a delignification aid than formic acid. A better result was obtained when both hydrogen peroxide and formic acid were added to the hydrotropic solution. Pulp produced by this combined treatment resulted in the lowest lignin content (kappa number). On the other hand, the pulps from the modified treatments had lower viscosities (Table 3), following a similar trend as kappa numbers, except for H and F pulps. The results showed that the additives accelerated both desired (delignification) and undesired (carbohydrate degradation) reactions, though at a different rate. Comparing the selectivity of the treatments, which can be expressed as a ratio of viscosity to kappa number, HF and H were much more selective than R and F treatments (Table 3).

Table 3. pH Values of Spent Solutions and Properties of Pulps from Reference and Modified Hydrotropic Treatments

	Treatment/Pulp *			
	R	H	F	HF
pH of hydrotropic solution				
Before treatment	9.3	8.9	3.4	3.5
After treatment	3.5	3.6	3.5	3.5
Yield, %:				
Total	47.6	47.5	45.1	43.5
Screened	47.3	46.8	45.0	43.2
Rejects	0.3	0.7	0.1	0.3
Viscosity, mL/g	1136	958	849	660
Kappa number	26.6	13.6	17.7	8.2
Viscosity/Kappa	42.7	70.5	48.0	80.1
Lignin, %	4.2	2.3	2.4	1.4
Xylose (anhydrous), %	6.5	6.8	4.6	5.0
Mannose (anhydrous), %	0.6	0.6	0.4	0.5
Cellulose yield (on wood), %	39.8	39.6	40.2	39.0

* R = Reference; H = H_2O_2; F = Formic acid; HF = H & F together

The effect of pH has been discussed by other researchers (Gromov and Odincov 1957a; Hinrichs *et al.* 1957; Kalninsh *et al.* 1967). The cited authors found that an increase of pH inhibits delignification and carbohydrate degradation reactions and a decrease of pH accelerates them. This supports the results obtained for F and HF pulps in comparison with R and H pulps, respectively.

The improvement caused by the addition of hydrogen peroxide can be explained by its delignification action. In acidic media, it forms a hydroxonium cation (Lachenal 1996; Gierer 1982), which is an electrophile and attacks the electron-rich sites of lignin, initiating such reactions as: ring hydroxylation, oxidative demethylation, oxidative ring opening, displacement of side chains, cleavage of β-aryl ether bonds, and epoxidation (Gierer 1982). The reduced viscosity of the pulps from hydrogen peroxide-aided treatments is presumably due to the formation of harmful radicals induced by high temperature and transition metals present in wood (Lachenal 1996).

No hexenuronic acid was detected in the pulps. This is in a good agreement with the general knowledge about hexenuronic acid formation, which takes place during alkaline pulping processes (Potthast 2006).

The results of acid methanolysis and GC (Table 3) revealed that the hydrotropic treatments removed a significant part of the hemicelluloses from birch wood. This is a consequence of hydrolytic processes induced by liberated organic acids, mainly acetic and formic acid (Gromov 1963; Nelson 1978). In the case of F and HF treatments, the reactions were enhanced by formic acid that was added to the hydrotropic solution. The pulps produced by the hydrogen peroxide-assisted treatments had a slightly higher content of hemicelluloses in comparison with the corresponding treatments without hydrogen peroxide.

The yields of the pulps from the modified treatments were lower than the yield of the reference pulp. Within the modified treatments, the pulp yields decreased in the sequence of H > F > HF (Table 3). However, the cellulose yields calculated on the original wood basis were almost equal for R, H, and F pulps, and 1% lower for HF pulp compared with the reference (Table 3). This means that the difference in the yields was mainly affected by the presence of components other than cellulose.

Generally, all modifications made the hydrotropic treatments more efficient and presented a possibility for their optimization by altering the treatment parameters and dosages of the chemicals. However, the addition of extra chemicals will result in higher costs of such treatments. From this point of view, the F treatment seems to be an interesting option. As mentioned earlier, a hydrotropic solution can be used up to 5 or 6 times before recovery. In the case of an unmodified process, the first treatment starts at an alkaline pH and the subsequent treatments are acidic, since the recycled spent solution from the first treatment has an acidic pH (see pH values in Table 3). This will result in treatments with different pH and, consequently, different pulp quality. To have consistent processes, either the hydrotropic solution for the first treatment must be acidified or the pH of the spent solutions must be adjusted to alkaline prior to treatments. The former seems to be a more attractive option due to the pulp characteristics. Moreover, if the pH is adjusted to alkaline, the alkali will be consumed by the organic acids that are released from the wood during the treatment. Consequently, build-up of the alkali-metal salts will cause complications in the recovery of the hydrotropic solution (Procter 1971). In this case, acidification would be a preferred measure to control the pulp quality.

Oxygen Delignification and Bleaching

Oxygen delignification reduced the kappa number of the reference and HF pulps to 16.3 and 4.4 units, respectively, which corresponds to delignification degrees of 39% and 46%. Viscosity also decreased in the course of oxygen delignification and became 1002 mL/g and 617 mL/g for the reference and HF pulps, correspondingly.

Overall consumption of hydrogen peroxide during bleaching was lower in the case of HF pulp (Table 4). Owing to a lower initial kappa number, a shorter retention time in the PO stage was required for HF pulp to reduce the kappa number to 1-2 units, and, consequently, less hydrogen peroxide was consumed in this stage. During the last bleaching stage, the consumption was nearly equal for both pulps (Table 4).

Table 4. Hydrogen Peroxide Consumption in PO and P Stages, and the Total in Bleaching

	Pulps	
	R	HF
PO stage, kg/t o.d. pulp	32.7	10.4
P stage, kg/t o.d. pulp	20.1	21.3
Total in bleaching, kg/t o.d. bleached pulp	56.3	33.2

A longer retention time in the PO stage resulted in an unexpected, considerable viscosity loss for the reference pulp, so the viscosity values of both pulps became almost equal after that stage (Table 5).

With the applied bleaching sequence, the pulps did not reach a high brightness (Table 5), which is usually close to or exceeds 90% ISO for dissolving pulps (Sixta and Borgards 1999; Sixta *et al.* 2004; Schild and Sixta 2011). However, bleaching optimization was not a purpose of this work. Information about hydrotropic pulp bleaching is rather limited, and only a few references can be found, so the topic must be researched further in order to carry out optimization and develop new, more efficient sequences.

The total yield of the HF-bleached pulp was lower than that of the bleached reference pulp by almost 3 percentage points. This was affected by the difference in the cooking yields, which was around 4 percentage points (Table 3). However, this difference was partially compensated by a lower content of non-cellulosic polysaccharides and a higher content of cellulose in HF pulp (Table 5).

Table 5. Pulp Properties after PO and P Stages

	Pulps	
	R	HF
After PO stage		
Kappa number	2.4	1.3
Viscosity, mL/g	588	578
Brightness, % ISO	76.0	77.9
After P stage		
Total yield, %	41.4	38.7
Viscosity, mL/g	562	542
Brightness, % ISO	87.5	87.9
Xylose (anhydrous), %	3.9	2.6
Mannose (anhydrous), %	0.4	0.2
Cellulose, %	93.0	96.9

Based on the viscosity values and the content of hemicelluloses, the pulps were comparable with other dissolving pulps found in the literature (Sixta and Borgards 1999; Sixta *et al.* 2004; Sixta 2006; Schild and Sixta 2011).

HCl/EtOH Pretreatment and Dissolution

The bleached HF pulp could not be dissolved in a 7% NaOH/12% urea/water mixture. The solution still contained fibres after it was kept in a cooler for 1 h. The 7% NaOH/12% urea aqueous solution has certain advantages as a cellulose solvent, being cheap and environmentally friendly. However, the solubilisation capacity is limited to cellulose samples that have a degree of polymerisation lower than a certain threshold value (Wang 2008) or have remnant primary wall fragments removed (Trygg and Fardim 2011). The same result was observed when an attempt was made to dissolve commercial sulphite dissolving pulp with a viscosity of 530 mL/g. To reduce the viscosity and remove a residual primary wall, HF pulp was treated with a HCl/EtOH mixture. The viscosity after the treatment dropped to 142.4 mL/g, and the pulp could be successfully dissolved to form clear solutions at concentrations of 0.2 to 5%.

The rheological studies revealed that the pretreated pulp was dissolved completely at concentrations of 0.2 to 3%, based on the growth of the apparent activation energy with the increase of cellulose concentration in the solution (Fig. 2). Conversely, the decrease of the activation energy at concentrations higher than 3% implies that the cellulose macromolecules in the solution form aggregates and inclusion complexes rather than existing in a free form (Roy *et al*. 2003; Trygg and Fardim 2011). Similar behaviour in the range of 0 to 100 s^{-1} shear rates was exhibited by the HCl/EtOH-pretreated sulphite dissolving pulp dissolved in a 7% NaOH/12% urea aqueous solution, although it could be dissolved completely up to 4% concentration at a high shear rate (1000 s^{-1}) (Trygg and Fardim 2011).

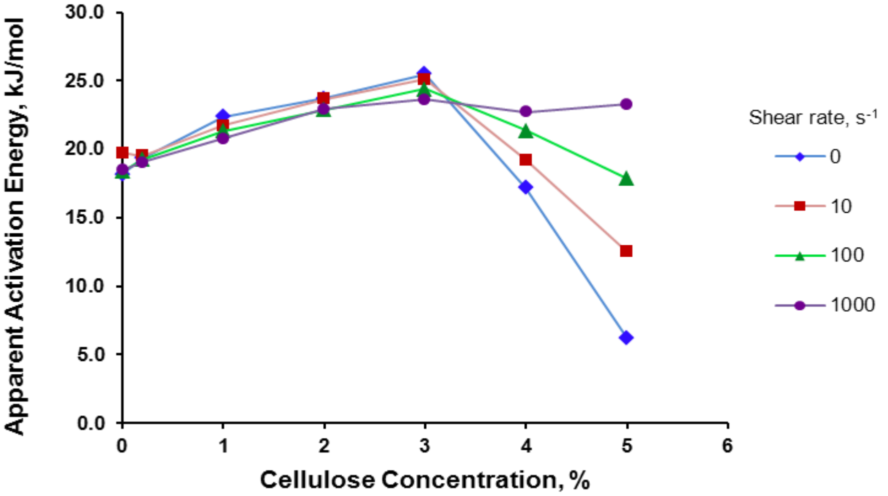

Fig. 2. Apparent activation energy for viscous flow *vs*. concentration of cellulose in a 7% NaOH/12% urea aqueous solution calculated at different shear rates

Isolation of Lignin and its Properties

Based on the precipitation experiment, the lignin concentration in the spent solution from the reference pulping was estimated to be 35.6 g/kg. Considering this value and a mass balance, the theoretical amount of recovered lignin was 161 kg/t o.d. wood (Table 6). However, it was not possible to remove all of the spent solution from the digester after treatment. Approximately 40% of it was retained in the chips and was removed from the pulp during the washing step. Hence, under laboratory conditions it was only possible to recover 97 kg lignin/t o.d. wood (Table 6). This value corresponds to

42% of the original lignin contained in the birch wood or 46% of the lignin dissolved during the treatment.

Table 6. Theoretical and Experimental Yields of Lignin Recovered from Spent Solution after Reference Treatment

	In the experiment	Based on calculations (theoretical)
Amount of spent solution, g	1633.3	2713.0*
Lignin from the spent solution, g	58.1	96.6
Yield, kg/t o.d. wood	97	161
Yield, % based on lignin in birch wood	42.0	69.8
Lignin dissolved during the reference treatment, g	126.4	
Yield, % based on dissolved lignin	46.0	76.4

*calculated as a sum of the amounts of water in the wood, hydrotropic solution, and dissolved wood

Even if the separation of spent solution had been complete, the amount of lignin recovered would have constituted only 70% of the lignin contained in the birch wood or 76.4% of the dissolved lignin (Table 6). A certain, presumably small, portion of the remaining 23.6% was lost during the washing of lignin. The rest of the unrecovered lignin can be explained by the fact that some part of the dissolved lignin did not precipitate upon dilution with water and stayed in the liquid phase (practically diluted sodium xylenesulphonate solution). Similar results were obtained by Gromov in studies of hydrotropic treatment of aspen wood at different temperatures and dwelling times (Gromov and Odincov 1957a). In his experiments, the portion of non-precipitated lignin was 24%, based on dissolved lignin, when the lignin was precipitated by 10-fold dilution of the spent solution obtained at the most severe cooking conditions (temperature 160 °C and dwelling time 6 h). According to Gromov and Odincov (1957a and b), this lignin fraction is composed of low molecular weight lignin, and it can be isolated by, for example, heating the liquid phase after lignin precipitation in the presence of acids. The quantity of non-precipitated lignin decreases with increasing cooking temperature and/or retention time (Gromov and Odincov 1957a). Another important factor that affects the amount of non-precipitated lignin is the ratio of spent solution to dilution water during precipitation. More lignin is precipitated when more water is added (Korpinen and Fardim 2009).

Due to extensive hydrolytic reactions during treatment, hemicelluloses were, to a great extent, removed from the lignin fraction (Table 7). The small amount retained in the lignin can be explained by the presence of covalent bonds between lignin and carbohydrates, the so-called lignin-carbohydrate complex. The most abundant “contaminating” carbohydrate was xylose or its polymeric form, which was an expected result since xylan is the main non-cellulosic polysaccharide of birch wood (see **Materials**).

Table 7. Carbohydrates in Hydrotropic Lignin Sample (as Anhydrous Units, %)

Ara	Xyl	Rha	Man	Glc	Gal	GlcA	4-O-Me-GlcA	GalA	Total
0.00	0.33	0.02	0.03	0.05	0.02	0.01	0.03	0.01	0.48

Ara – arabinose, Xyl – xylose, Rha – rhamnose, Man – mannose, Glc – glucose, Gal – galactose, GlcA – glucuronic acid, GalA – galacturonic acid

The sulphur content of lignin was 0.22%. This was in contrast with the previously reported findings of Gromov and Odincov (1957a), where no sulphur was detected in the hydrotropic lignin sample. It is generally believed that hydrotropic agents do not chemically react with lignin (Gromov 1963; Procter 1971), so the source of sulphur can be attributed to a hydrotrope that was not completely removed during the washing of lignin. The difference in results can be explained by the different washing procedures applied in the cited reference and in this study.

The obtained lignin sample had a lower content of carbohydrates than other technical lignins: kraft (1.0 to 2.3%), soda (1.5 to 3.0%), hydrolysis (10.0 to 22.4%), organosolvent (1.0 to 3.0%) (Vishtal and Kraslawski 2011), and lignosulphonates (6.8 and higher (Leger *et al.* 2010)). The sulphur content was lower than that of lignosulphonates (3.5 to 8.0%) and kraft lignins (1.0 to 3.0%), but higher than organosolvent and soda lignins, which are sulphur-free (Vishtal and Kraslawski 2011). The low content of carbohydrates and sulphur makes hydrotropic lignin a valuable raw material for different applications or for further thermal and chemical conversion.

CONCLUSIONS

1. The present study showed that a conventional hydrotropic treatment can be improved by the addition of formic acid, hydrogen peroxide, or both simultaneously. The pulps obtained by the modified treatments had lower lignin contents. The overall selectivity was higher for the modified treatments than for the reference. This provides the possibility for further optimization of the process by altering the process conditions. The addition of formic acid resulted in greater removal of hemicelluloses, which is advantageous for dissolving-grade pulps.
2. The bleached pulps had a high content of cellulose and low content of hemicelluloses. Considering these parameters and the viscosity values, the bleached pulps were comparable to various dissolving pulps described in the literature. However, with the applied bleaching sequence the pulps did not reach high brightness level typical for dissolving pulps. The bleaching procedure needs to be studied further in order to develop more efficient bleaching sequences.
3. HCl/EtOH-pretreated bleached pulp with the lowest content of hemicelluloses could be completely dissolved in 7% NaOH/12% urea aqueous solution at up to a 3% cellulose concentration. At the concentrations of 4 and 5%, the cellulose macromolecules formed aggregates and inclusion complexes; however, the solutions were transparent. In the range 0 to 100 s^{-1} shear rates, the rheological behaviour of the obtained solutions was similar to that of HCl/EtOH-pretreated sulphite dissolving pulp dissolved in the same solvent.
4. Recovered and washed hydrotropic lignin had a low content of hemicelluloses in comparison with other technical lignins such as, kraft, soda, hydrolysis lignin, and lignosulphonates. The sulphur content was lower than in kraft lignin and in lignosulphonates.

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