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Mass transport and yield during spinning of lignin-cellulose carbon fiber precursors

Abstract: Lignin, a substance considered as a residue in biomass and ethanol production, has been identified as a renewable resource suitable for making inexpensive carbon fibers (CFs), which would widen the range of possible applications for light-weight CFs reinforced composites. Wet spinning of lignin-cellulose ionic liquid solutions is a promising method for producing lignin-based CFs precursors. However, wet-spinning solutions containing lignin pose technical challenges that have to be solved to enable industrialization. One of these issues is that a part of the lignin leaches into the coagulation liquid, which reduces yield and might complicate solvent recovery. In this work, the mass transport during coagulation is studied in depth using a model system and trends are confirmed with spinning trials. It was discovered that during coagulation, efflux of ionic liquid is not hindered by lignin concentration in solution and the formed cellulose network will enclose soluble lignin. Consequently, a high total concentration of lignin and cellulose in solution is advantageous to maximize yield. This work provides a fundamental understanding on mass transport during coagulation of lignin-cellulose solutions, crucial information when designing new solution-based fiber forming processes.

Keywords: biomass, carbon fiber, ionic liquids, lignin, wet spinning

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Introduction

Carbon fibers (CFs) are one of the man-made fibers with the highest specific strength and stiffness, which makes them very efficient reinforcements in composite materials for light-weight applications, such as transport and construction. The production of CFs requires a polymeric precursor fiber that later can be carbonized up to a carbon content of at least 92 wt% (Frank et al. 2014). For this reason, a high initial carbon content in the precursor is preferable to be able to reach a high yield in CFs production. Today, CFs are predominately made from polyacrylonitrile (PAN) fibers, a fossil-based wet-spun precursor. PAN-based CFs exhibit excellent mechanical properties with tensile strengths up to 7 GPa. Unfortunately, PAN fibers are relatively expensive, which renders a CFs price that hinders extensive use in cars and other mid-range products (Ogale et al. 2016). Consequently, an inexpensive precursor that enables high yield conversion into CFs, and that is preferably bio-based, is needed to expand the market for CFs. CFs are also produced from regenerated cellulose, however, only covering less than 2% of the global market (Dumanlı and Windle 2012) due to low yields when converted into CFs (Spörl et al. 2017).

Lignin, the second most abundant macromolecule on Earth, is today an underutilized bioresource (Gellerstedt and Henriksson 2008). Its aromatic structure results in high carbon content, and lignin is, therefore, considered to be a promising raw material for CFs (Ragauskas et al. 2014). Lignin constitutes between 20 and 30 wt% of the dry mass in softwood. About 100 million tons of softwood is harvested annually and fractionated predominantly with the kraft process (Gellerstedt 2015). In this pulping process, however, lignin is most commonly spent as fuel by incineration in the recovery boiler. This approach results in low raw material utilization (40–55%) as only carbohydrates are recovered for further valorization. Additionally, the recovery boiler often limits the capacity of the mill (Gellerstedt et al. 2010). Both of these issues, low yield and capacity limit, could be improved by extracting a fraction of the lignin from the process for further utilization, e.g. through the LignoBoost process. In the LignoBoost process, lignin is precipitated from the black liquor of the kraft pulping process by lowering of the level of pH with carbon dioxide (Wallmo 2008).

LignoBoost lignin is, in contrast to cellulose, thermoplastic, which allows the continuous fibers to be shaped through melt spinning. This property was utilized as early as in the 1960s when lignin-based CFs were commercialized under the brand "Kayacarbon". However, production and development ceased during the next decade due to the better performance of synthetic polymers (Frank et al. 2014). More recent research on melt spinning of lignin has not yet found sufficient mechanical properties for industrial application and the lignin fibers are very brittle (Baker and Rials 2013). Consequently, lignin alone might not be sufficient as a raw material for CFs.

The concept of lignin-based CFs has recently attracted new interest through the idea of combining the advantages of lignin with the advantages of cellulose: yield and strength (Ma et al. 2015; Garoff et al. 2017; Olsson et al. 2017; Vincent et al. 2018). Cellulose contributes to the strength of the precursor fibers, while lignin, with the higher carbon content of the two, increases the yield (Bengtsson et al. 2018). Such fibers can be created by wet spinning mixed solutions in which lignin and cellulose are first dissolved in a common solvent and then precipitated in a coagulation bath.

The main issue when using a wet-spinning method to produce lignin-cellulose-based fibers is that lignin and cellulose have different solubility characteristics. Lignin is soluble in various solvents to a far greater extent than cellulose (Casas et al. 2011), which poses a problem to the coagulation step. In a previous study, we reported the loss of low-molecular-weight (MW) lignin in an aqueous coagulation bath during wet spinning (Bengtsson et al. 2018). Despite that the leached fraction is small, it remains important to minimize this loss. Leached lignin could be problematic for two reasons: to avoid yield loss and to avoid the accumulation of impurities in the spin-bath; the latter may complicate solvent recovery. Therefore, it is crucial to understand the mass transport during coagulation for further development of this process. The total mass transport includes both the diffusive mass transport of solvent out of the solution and non-solvent into the solution as well as lignin leaching out of the solution.

Only a few studies on measuring the lignin content of wet-spun lignin-cellulose fibers have been reported previously in the literature. Ma et al. (2015) attempted to measure the lignin content of filaments using X-ray photoelectron spectroscopy (XPS) analysis. However, no clear correlation between added kraft lignin and lignin content in filaments was established. Garoff et al. (2017) estimated the lignin content with elemental analysis using sulfur, taking advantage of the fact that kraft lignin precipitated from black liquor will carry some sulfur. They found

that the filaments from an N-methylmorpholine-N-oxide (NMMO) solution containing equal amounts of cellulose and lignin coagulated in deionized water (DW) had a lignin content as low as 28%. However, when a calcium salt ($CaCl_2$) was added to the coagulation bath, the lignin content of filaments increased to 43%. These findings emphasize the need to further study the correlation between lignin yield and coagulation liquid composition.

Lignin leached during coagulation can be quantified using ultraviolet (UV) absorption at 280 nm. However, it is impractical to measure leached lignin during actual spinning. Consequently, a model system is necessary to thoroughly study lignin leaching during coagulation. In this work, the lignin leaching from membranes immersed into different coagulation liquids is studied over a timescale that covers both the initial coagulation and the washing stage. The method used was developed by Hedlund et al. (2017) to study mass transport during cellulose coagulation. By using this method, it is also possible to determine the efflux of solvent from coagulating lignin-cellulose solutions. Determining the solvent efflux is important because it is the ratio of lignin leaching rate and solvent wash-out rate that determines the lignin yield given a certain level of solvent recovery. The aim of the work was to investigate the influence of coagulation liquid composition and the solid content (SC) of solution on lignin leaching with the goal of understanding how to improve lignin yield in spun fibers.

Materials and methods

Materials: Softwood kraft lignin (SKL) was received from Bäckhammar Pilot Plant (RISE, Bäckhammar, Sweden) where it was isolated through the LignoBoost method using industrial black liquor. The steps of LignoBoost include lowering the pH level with carbon dioxide to about pH 10. The filtrated precipitate is thereafter re-suspended at pH 2–3 using sulfuric acid. The precipitate is then filtered a second time and washed in slightly acidic water. Detailed information on the purity of SKL, including sugar content, is available in Bengtsson et al. (2018), where the ash content was also determined to be below 1%. Before use, SKL was dried overnight in 60°C at 10 kPa. A softwood kraft dissolving pulp (DKP) [intrinsic viscosity of 465 ml g⁻¹ according to International Organization for Standardization (ISO) 5351:2010] was purchased from Georgia Pacific Cellulose (Atlanta, GA, USA). Pulp sheets were chopped, ground and dried overnight at 40°C prior to dissolution. The solvent, 1-ethyl-3-methylimidazolium acetate (EMIMAc, Aldrich 95%), was used as received. The acids used to lower the pH level in coagulation liquids were acetic acid (Aldrich, Steinheim, Germany, ≥99.5%) and sulfuric acid (VWR, Radnor, PA, USA, 95%).

Dissolution: Lignin and cellulose were dissolved simultaneously in neat EMIMAc at 70°C for 1 h in a closed reactor with overhead stirring

at 30 rpm. Two SCs of solution were prepared, 18 and 27 wt%, with a constant lignin:cellulose ratio of 70:30. The upper practical limit for the membrane method, due to its high viscosity, was the higher concentration of 27%; however, this was not the limit of solubility in the EMIMAc solvent. Complete dissolution was confirmed by observing the solutions in light microscopy using crossed polarizers (Nikon Eclipse Ci-POL, Nikon Instruments, Tokyo, Japan). Deaeration was done at 60°C at a pressure below 10 kPa for at least 5 h prior to coagulation measurements. A reference sample containing only cellulose, 5.4 wt%, was dissolved using the same procedure.

Membrane coagulation method: Membrane coagulation was applied as a model system for filament coagulation during wet spinning, illustrated in Scheme 1. The method is described in detail in a previous publication (Hedlund et al. 2017). In short, a well-defined tube-shaped membrane, 0.35 mm thick and 58 mm long, was coagulated in a stirred coagulation bath with known mass, ca 33 g with an accuracy of 0.0001 g. A total of 10–12 measurements were performed with residence times from 3 s up to 72 h for each set of SC and type of coagulation liquid. After removal from the coagulation bath, the membranes were put in new vials filled with DW, close to 12 g with an accuracy of 0.0001 g, for at least 3 days (hereinafter denoted as washing bath). Three different conditions in the coagulation bath were investigated: acidity and solvent content [15% EMIMAc (15%E)], as well as a combination of the two. A coagulation bath containing EMIMAc was included as this situation would occur in industry, which applies counter-current washing of fibers. To limit the energy demanded during solvent recovery, the solvent content should be as high as possible (White 2001), and 15%E was chosen therefore. Pure MilliQ water was used as the reference. An initial test showed that a higher maximum draw ratio during spinning was possible if the coagulation bath had a low temperature; for this reason, the

coagulation bath temperature was kept at 5 ± 1°C. This observation is also in line with what has been found for similar solvent systems (Hauru et al. 2014). The acidic coagulation baths contained either acetic acid (0.6 or 12 wt%, pH of 4 and 2.4, respectively) or sulfuric acid (0.02 or 0.4 wt%, pH 2.4 and 1.3). The combination of EMIMAc and acetic acid (15%E, 12% acetic acid) reached pH 4. Leached lignin was quantified through UV absorbance (using Specorde 200 Plus, Analytic Jena, Jena, Germany) at 280 nm converted to g l^{-1} with the Lambert-Beer law using the extinction coefficient of 24.6 l g^{-1} cm^{-1} (Fengel et al. 1981). The conductivity of the same baths was measured (at 23°C, using Cond 720, inoLab, Benchtop Conductivity Meter, Thomas Scientific, Swedesboro, NJ, USA) to quantify the EMIMAc concentration. A linear calibration curve was constructed from six measurements from 0.1 to 0.5 wt% EMIMAc. To obtain results within calibration, <2 mS cm^{-1}, the coagulation baths were diluted with DW if necessary, which was accounted for in the quantification.

Apparent soluble fraction of SKL: The apparent soluble fraction of dry SKL powder and SKL dissolved in EMIMAc was analyzed for each coagulation liquid composition. SKL, both in the form of dry powder and 12.6% SKL in EMIMAc, was mixed into each coagulation bath to a final concentration of 0.13% lignin, equal to the amount of lignin in membranes. Insoluble lignin was filtered (Whatman GF 8) off the dry added SKL. The same procedure was not suitable, however, when solutions of lignin were added as the result was turbid filtrates. For this reason, these mixtures were centrifuged at 4000 rpm for 10 min. The soluble fraction of dry and dissolved SKL was quantified on filtrate and supernatant, respectively, using UV/visible (UV/Vis) absorbance as described earlier.

Calculation of diffusion coefficients: Apparent diffusion coefficients were calculated using the same methodology as applied by
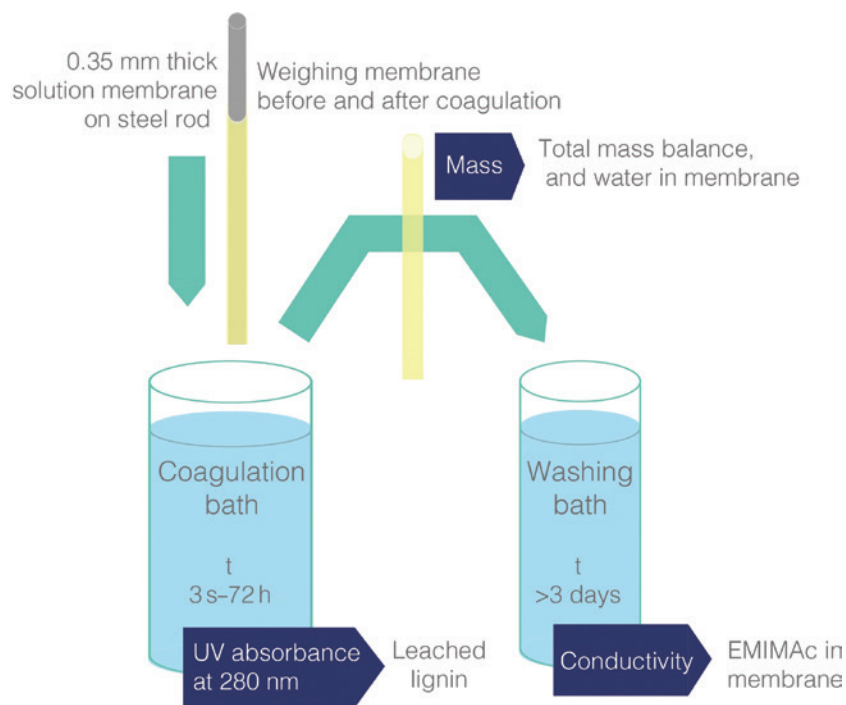
Scheme 1: Illustration of the membrane coagulation method.

Hedlund et al. (2017). If short times are considered, when the EMIMAc concentration adjacent to the steel rod can be considered constant, coagulation can be described by the equations of Fickian diffusion into an infinite slab in a single dimension. The efflux of EMIMAc was found from the amount of EMIMAc that remained in the membrane after a certain time, given by the concentration of EMIMAc in the washing bath measured with conductivity. The final diffusion coefficients were calculated as the average of the time range used, $15 < t_i < 240$ s, according to Eq. 1. The time range was based on the requirement that the ratio $\frac{M_i(t)}{M_{i\_tot}}/\sqrt{t_i}$ had not yet started to decline from its initial plateau level, typically when $\frac{M_i(t)}{M_{i\_tot}} < 0.7$.

$$D_i = \frac{\pi}{t_i}\left(\frac{M_i(t)}{M_{i\_tot}}\frac{d}{2}\right)^2 \qquad (1)$$

In Eq. 1, D is the diffusion coefficient in $m^2\,s^{-1}$, t is the time in seconds and d is the thickness of the membrane in meters corrected for the curvature of the membrane (Hedlund et al. 2017). $M(t)$ is the mass of EMIMAc diffused out from the membrane after time t, normalized against M_{tot}, the mass of EMIMAc diffused out after 60 000 s (Crank 1975).

Spinning trials: Solutions with 18 or 27% SC of solution were spun using bench-scale spinning equipment consisting of a piston pump, a coagulation bath (5 l) and a take-up roll. The spinneret had 33 holes with a capillary diameter of 120 μm and length to diameter (L/D) 2. The extruded solution filaments were stretched 4 times in an air gap of 10 mm and coagulated in an aqueous spin-bath at 5°C with either neat DW or with the addition of 15%E. The filaments were, subsequently, washed in either DW or dilute acid (0.02% sulfuric acid, pH 2.4) for 24 h and treated with fabric softener (cationic surfactant), for improved handling, before drying at 80°C for 45 min.

Lignin content of spun fibers: Lignin leached during spinning was determined through a mass balance of the spinning system. All coagulation and washing liquids were weighed. The leached lignin and EMIMAc for each bath were quantified according to methods described in the Membrane coagulation method section. The mass of solution that passed through the coagulation bath was determined by weighing the dope container before and after spinning. The mass of filaments in each washing bath was noted, and the lignin content of dried fibers was estimated from the lignin mass balance.

The lignin content of the added raw materials, SKL and DKP, and of the spun filaments was analyzed using chemical analysis. Klason lignin was determined gravimetrically as the solid residue after complete hydrolysis in 72% sulfuric acid. Acid soluble lignin was calculated from the absorbance of hydrolysate at 205 nm using an extinction coefficient of 110 l g^{-1} cm^{-1} (Theander and Westerlund 1986).

Results and discussion

The membrane method allowed the diffusion of EMIMAc to be tracked, as well as the leaching of lignin and the inward diffusion of water. Lignin leached during coagulation was compared to dissolved lignin when lignin, either as a dry powder or dissolved in EMIMAc, was added to the same coagulation liquid composition, Finally, a few spinning trials were performed to evaluate the applicability of the model results.

Diffusion of EMIMAc

The diffusion coefficients of EMIMAc were calculated based on the amount of residual EMIMAc that could be extracted from the model tubes by the washing baths. Figure 1 shows that, for the same coagulation liquid, no significant differences were seen among EMIMAc diffusion coefficients for the different SCs of solution. Neither did the complete omission of lignin have a significant effect on the coefficient of EMIMAc diffusion. The observation that the coefficient of EMIMAc diffusion is independent on SC is consistent with the observations made by Hedlund et al. (2017) who investigated neat cellulose-EMIMAc solutions. They proposed that the inflow of water causes cellulose to precipitate into an aggregated fibril network and enable the desorption of EMIMAc from cellulose. They further suggested that during coagulation, the diffusion of EMIMAc and water takes place in the open pores formed by the cellulose fibrillar network. Subsequently, EMIMAc diffusion is independent of cellulose concentration in the initial solution. Lignin does not crystallize like cellulose and has a higher solubility in EMIMAc than cellulose. Consequently, lignin is not expected to separate from solution into a distinct solid phase. Therefore, a higher SC of solution was expected to impede EMIMAc diffusion through lignin-EMIMAc interactions, which was not the case and makes the results in this study particularly interesting.

High EMIMAc concentrations in EMIMAc-water mixtures reduce the diffusivities of both water and EMIMAc, but at 15 wt% (<2 mol%), the effect on diffusivity is minor (Hall et al. 2012). This explains why a decrease in the apparent diffusion rate was not observed when a coagulation
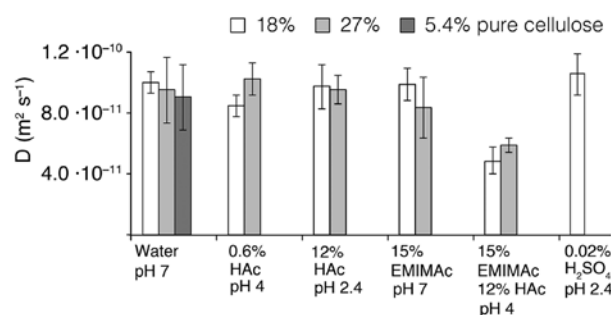

Figure 1: Diffusion coefficients for EMIMAc during coagulation in different coagulation baths for the two solid contents of solution.

Table 1: Compilation of used coagulation baths.

Conditions in coagulation bath	Soluble fraction of SKL (dry powder)	Soluble fraction of SKL (12% solution)	18% SC, lignin leached after 6000 s	27% SC, lignin leached after 6000 s
MilliQ water, pH 7	1.6%±0.4%	5.9%±0.5%	2.8%±0.3%	2.0%
0.6% Acetic acid, pH 4	2.1%	6.2%	2.9%	2.0%
12% Acetic acid, pH 2.4	4.2%	10.0%	4.5%	3.1%
15% EMIMAc, pH 7	5.4%	13.0%	5.2%	4.0%
15% EMIMAc, 12% Acetic acid, pH 4	13.3%	26.3%	9.6%	7.1%
Sulfuric acid, pH 2.4	1.1%	5.6%	2.8%	–
Sulfuric acid, pH 1.3	0.9%	4.4%	2.2%	–

Soluble fraction of dry SKL powder and SKL that was first dissolved in EMIMAc and then precipitated, and leached lignin after 6000 s from membranes with the two solid contents of solution.

liquid contained EMIMAc. A decrease in the EMIMAc diffusion coefficient was, on the other hand, observed when the coagulation liquid contained both EMIMAc and acetic acid. Table 1 shows that the combination of EMIMAc and acetic acid enables the highest soluble lignin fraction, and perhaps this is part of the explanation of the lower diffusion coefficient. When this combination of EMIMAc and acetic acid is used, it allows a high concentration of lignin in the liquid phase inside the pores of the coagulated cellulose network. The dissolved lignin probably interacts with EMIMAc and inhibits diffusion. In other coagulation baths, in which the solubility of lignin is lower, essentially all of the lignin will be precipitated from the coagulation liquid and adsorbed on the cellulose network and, consequently, will not interfere much with EMIMAc diffusion.

Water diffusion coefficients were calculated from the mass before and after immersion in the coagulation liquid. The softness of the membranes, however, made them sensitive to the slight pressure applied when the excess coagulation liquid was wiped off the surface before weighing. Consequently, the diffusion coefficients for water are associated with an uncertainty and are, therefore, presented in the Supplementary Information (SI), Figure 1S. Despite measurement difficulty, a few observations were made; water diffusion coefficients were approximately constant irrespective of SC of solution and coagulation liquid composition. If compared to diffusion coefficients for EMIMAc, D_{water} was 2.0 ± 0.2 times higher than D_{EMIMAc}, which increased to 3.1 ± 0.1 when the coagulation liquid contained both EMIMAc and acetic acid. The increase in ratio once more indicates an interaction between dissolved lignin and EMIMAc as water is typically not affected by dissolved polymers at moderate concentrations.

In the studied cases, these relations indicate that water precedes EMIMAc diffusion during coagulation, and both diffusivities are independent of the SC of the solution. Hedlund et al. (2017) also measured the coagulation

rate of cellulose solutions and found it to be correlated to non-solvent diffusion. The coagulation rate of lignin-cellulose solutions was not measurable using optical methods due to its dark color. However, if that conclusion is transferred to the present findings, it indicates that the coagulation rate of lignin-cellulose solutions is independent of SC in the studied range.

Leaching of lignin

Figure 2 presents absolute amounts of lignin leached from membranes coagulated for certain times. Leaching of lignin is clearly more pronounced when EMIMAc is present in the coagulation bath than if pure MilliQ water is used. The same is true for acetic acid. The amount of lignin leached from the membrane increases even further when the bath contains both EMIMAc and acetic acid.

The amount of lignin leached during coagulation correlates to the solubility of lignin in the coagulation liquid.
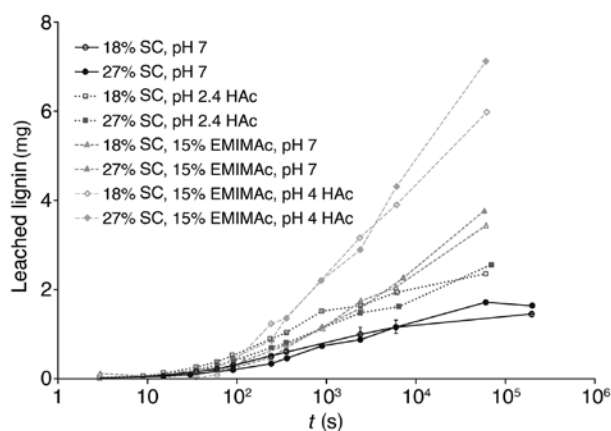
Figure 2: Absolute amounts of lignin leached into the coagulation bath after different amounts of time.
Standard deviations of measurements with 18% solid content in MilliQ water, $n = 3$.

Table 1 shows the apparent solubility of lignin as the fraction of SKL that goes into the solution after mixing with a certain coagulation liquid; this is for both dry powder and lignin dissolved in EMIMAc. The two dissolution methods gave different apparent solubility values. The difference can be attributed to kinetic effects; a slurry of powder compared to the mixing of two fluids, or the difference can be attributed to dissolved lignin remaining soluble if interactions with the solvent remain. Lignin is highly soluble in EMIMAc and, according to Zhang et al. (2017), the strongest interactions are H bonds between the acetate ions and the aliphatic hydroxyl groups in lignin. The cation can also form a π-stacking interaction with the aromatic ring in lignin. In Table 1, values from 6000 s were chosen as, at that time limit, the EMIMAc concentration in the coagulation bath no longer increased notably, as illustrated in Figure 2S in the SI.

In all coagulation liquids, the fraction of leached lignin after 6000 s is between the apparent soluble fraction of dry SKL and that of dissolved SKL. Consequently, leached lignin appears to be controlled by the solubility of lignin in the coagulation liquid. However, this observation also indicates that lignin is enclosed in one way or another during the coagulation of lignin-cellulose solutions, as less lignin will leach than is soluble when a pure lignin solution is coagulated.

Another systematic difference between the two SCs of solution is evident in Table 1. For a solution with a 27% SC, relatively less lignin will be leached in the same coagulation liquid. This relation is also shown in Figure 2 where the absolute amount of leached lignin between the two SCs of solution is plotted as a function of time. One plausible explanation is that the lignin solubility limit is reached in the liquid phase inside the pores formed during the coagulation of cellulose, which causes excess lignin to precipitate. Thus, a higher SC of solution would lead to the encapsulation of a larger fraction of the lignin and, consequently, a higher lignin yield. This finding combined with what we have shown, that a higher SC does not hinder EMIMAc diffusion in lignin-cellulose solutions, gives further reason to use maximal, yet spinnable, SC of solution when spinning lignin-cellulose fibers.

Contrary to what was initially expected, a low pH level showed no obvious benefit for the lignin yield, as shown in Figure 3. Rather it seems, that at short times, below 6000 s, when the EMIMAc continues to diffuse out of the membrane, the value of pH has no effect on leached lignin. This observation is visible in the black curves in Figure 3 where pH was reduced with sulfuric acid. Even more, when the bath was acidified with 12% acetic acid, it had a negative effect on lignin yield. Acetic acid supplies

some acetate ions to the solution, but most of the acetic acid, >98%, will be protonated at pH ≤4; nevertheless, acetic acid enhances lignin solubility. On the other hand, a fair assumption from Figure 3 is that equilibrium is not reached, apart from perhaps for membranes coagulated in pH 1.3 (sulfuric acid). When the lignin content of washing baths was analyzed, where the residence times were sufficient to reach equilibrium, a clear pH trend was found, as seen in Figure 4.

In an earlier study, the lower MW fraction of lignin was found to leach out into the coagulation bath (Bengtsson et al. 2018). Previous literature have reported an enrichment of carboxylic groups in low MW lignin (Bylin et al. 2014; Aminzadeh et al. 2018). In the case of lignin leached in washing baths, a clear trend toward less lignin leached can be found when the pH drops to a level of 4 or below in washing baths.

As is well known in pulping, charged lignin molecules are soluble in aqueous solutions and the base of delignification. Low pH levels result in the low ionization of lignin
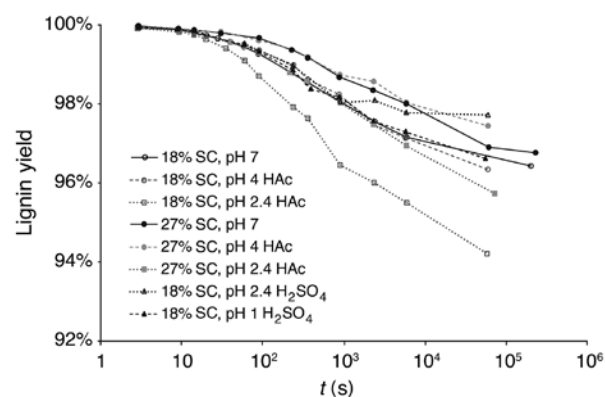

Figure 3: Leaching of lignin as a function of time in coagulation baths with different levels of pH.
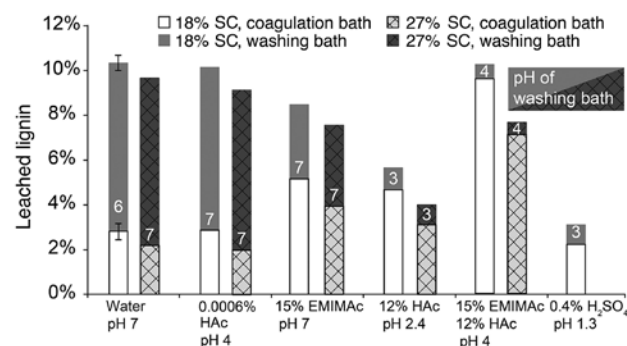

Figure 4: Lignin leached after 6000 s in the coagulation bath and in the washing bath after 3 days for different coagulation baths. White digits inside the washing bath bars indicate the level of pH.

Table 2: Lignin yield during spinning, and calculated and measured lignin content of spun fibers.

Sample, coagulation bath – washing conditions	Leached lignin, UV[a] (%)	Lignin content of filaments, (%) calculated from UV measurements	Klason lignin[b] (%)	Acid soluble lignin[c] (%)
Raw materials, SKL and DKP	–	–	65.8	4.3
Filament 18% SC, DW – neutral	6.2	68.6	65.8	1.3
Filament 18% SC, DW – acidic	4.7	69.0	66.9	1.9
Filament 18% SC, 15%E – neutral	7.6	68.4	64.1	1.9
Filament 18% SC, 15%E – acidic	6.1	68.7	65.5	2.1
Filament 27% SC, DW – neutral	7.3	68.6	64.6	1.7
Filament 27% SC, DW – acidic	4.0	69.4	65.7	1.5

Standard deviation of methods from duplicates: [a]0.4%, [b]1.1%, [c]0.1%.
Filaments were coagulated in either deionized water (DW) or 15% EMIMAc (15%E).

and, thereby, less solubility. Carboxylic groups in lignin have a pKa of around 4.4 (Ragnar et al. 2000); therefore, these results indicate the influence of the protonation of carboxylic groups on lignin yield. It should be mentioned that a reduction of pH is also associated with an increase in ionic strength, which is known to reduce the solubility of lignin (Lindström 1980). The lowest amount of leached lignin was found for tubes coagulated in baths acidified with sulfuric acid; the acidity was high enough to lower the pH in washing baths. Interestingly and not fully understood why, although gratifying, membranes that coagulated in 15%E leached less total lignin after washing than those coagulated in pure water.

Spinning lignin-cellulose filaments

Spinning trials were performed to confirm the applicability of the model results. Filaments were spun in either pure DW or with the addition of 15%E; the latter was to simulate the situation that occurs in counter-current washing. As a positive trend for a low level of pH was found for washing baths, a comparison was made between neutral and acidic washes. To evaluate the eventual degradation of filaments upon drying after an acidic wash, the mechanical properties of filaments were measured and are available in Table S1 in the SI. The mechanical properties of the fibers did not differ significantly between the fibers washed in neutral and acidic conditions, which indicates little or no degradation of cellulose.

A consistent difference was found when the UV absorbance was measured. Less lignin was leached in the acidic conditions, as shown in Table 2. It can further be seen that the filaments in all the samples washed in acidic conditions also contained more lignin, both Klason and acid soluble lignin. Also in correlation with model results,

more lignin will also leach if the coagulation bath contains 15%E. On the other hand, lignin leached from filaments was found to be less than the total amount of the lignin leached from membranes in Figure 4. As discussed in the Leaching of lignin section, membranes were left in wash baths until equilibrium; however, EMIMAc levels will even out before leaching of lignin cease. Therefore, lignin yield can be maximized if the washing time is optimized and interrupted once essentially all the EMIMAc has diffused out of the coagulated solution.

Conclusions

A higher SC of solution contributes to a higher yield of lignin during wet spinning. Consequently, it is beneficial to maximize SC of solution when lignin-cellulose fibers are spun. Efflux of EMIMAc will level out sooner than leaching of lignin cease. Washing should therefore be interrupted once essentially all the EMIMAc is removed to increase lignin yield.

The diffusion coefficients of EMIMAc and water are not significantly affected by the SC of solution during coagulation. Based on water diffusivity, the same relation holds true for the coagulation rate, which further promotes a high SC of solution.

The results from both the membrane method and the spinning trials indicate that a low level of pH in the coagulation bath gives a higher lignin yield. This trend was not evident in the initial stage of coagulation but after prolonged washing, however, a pH below 4 increased the lignin yield.

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