Lignin enhances cellulose dissolution in cold alkali

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ABSTRACT

Aqueous sodium hydroxide solutions are extensively used as solvents for lignin in kraft pulping. These are also appealing systems for cellulose dissolution due to their inexpensiveness, ease to recycle and low toxicity. Cellulose dissolution occurs in a narrow concentration region and at low temperatures. Dissolution is often incomplete but additives, such as zinc oxide or urea, have been found to significantly improve cellulose dissolution. In this work, lignin was explored as a possible beneficial additive for cellulose dissolution. Lignin was found to improve cellulose dissolution in cold alkali, extending the NaOH concentration range to lower values. The regenerated cellulose material from the NaOH-lignin solvents was found to have a lower crystallinity and crystallite size than the samples prepared in the neat NaOH and NaOH-urea solvents. Beneficial lignin-cellulose interactions in solution state appear to be preserved under coagulation and regeneration, reducing the tendency of crystallization of cellulose.

1. Introduction

Cellulose and lignin are the most abundant renewable resources in nature; they synergistically coexist as the main components of woody secondary cell walls. In secondary cell walls, tough microfibrils of cellulose are embedded in a highly crosslinked amorphous matrix of lignin and hemicelluloses. The microfibrils provide mechanical strength and rigidity to the plant cell walls while the matrix provides resistance to compression and hydrophobicity for transport functions (Zhong, Cui, & Ye, 2019). Lignin is a complex polyphenolic polymer that is typically obtained as a sub-product in chemical pulping processes to extract and purify cellulose fibers. Therefore, the lignin extracted from chemical pulping, especially from kraft pulping operations, is typically heavily degraded. Due to its relatively low molecular weight and the presence of contaminants, it is not surprising that most of it ends up being burned for energy generation at the pulp mill. Only ca. 1–2% of the 50–70 million tons of lignin produced annually, are being used to produce added value materials (Melro, Alves, Antunes, & Medronho, 2018; Melro, Filipe, Sousa, Medronho, & Romano, 2021; Norgren & Edlund, 2014). From a

structural point of view, lignin presents molecular functionalities of different polarity (e.g., hydrophobic aromatic rings and hydrophilic -OH moieties), just as cellulose. Such chemical structure anisotropy is expected to give rise to an amphiphilic behavior, which is evidenced by, for instance, its self-organization both in bulk solution and at interfaces (Costa et al., 2019; Costa et al., 2019; Lindman et al., 2017; Norgren, Edlund, & Wågberg, 2002; Rojas et al., 2007; Lizunda et al., 2021), in lignin-cellulase interactions, lignin-protein adsorption and surfactant-lignocellulose interactions in enzymatic hydrolyses (Börjesson, Engqvist, Sipos, & Tjerneld, 2007; Eriksson, Börjesson, & Tjerneld, 2002; Nakagame, Chandra, Kadla, & Saddler, 2011; Pareek, Gillgren, & Jönsson, 2013; Rahikainen et al., 2013). Cellulose amphiphilicity and the role of hydrophobic interactions in cellulose dissolution in aqueous systems (including NaOH-based ones) have been revisited during the last decade (Lindman, Medronho, Alves, Norgren, & Nordenskiöld, 2021). Its amphiphilic character is evidenced not only by its structural features but also by phenomena, such as its association with surfactants and the modification of the hydrophobic interactions by amphiphilic additives (Lindman et al., 2021). Additives, such as urea, thiourea, poly

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(ethylene glycol) and surfactants, as well as amphiphilic cations (e.g., tetrabutylammonium, TBA$^+$), have been suggested to weaken the hydrophobic interactions of cellulose, thus improving dissolution and delaying/preventing gelation of the dopes (Alves, Medronho, Antunes, Topgaard, & Lindman, 2016; Medronho et al., 2015; Medronho & Lindman, 2014). In view of the increasing attention to the role of amphiphilicity and ionization in cellulose manipulation, and dissolution in particular, there is a general interest in investigating additives of potential help. Like cellulose, lignin is an amphiphilic molecule and has a pH dependent ionization, and so, it is a natural candidate. The aim of the present work was to provide some initial insight into the effect of lignin on cellulose dissolution and regeneration.

Lignin charge is pH-dependent because of the presence of abundant phenolic groups. Similar to cellulose, lignin solubility is enhanced in solvents of intermediate polarity and by certain surfactants (Melro et al., 2018; Melro, Valente, Antunes, Romano, & Medronho, 2021; Norgren & Edlund, 2001). Previous studies have been reported regarding mixtures of cellulose and its derivatives with lignin to manufacture, for example, carbon fibers, films, beads, and porous materials (Bengtsson, Bengtsson, Sedin, & Sjöholm, 2019; Gabov, Oja, Deguchi, Fallarero, & Fardim, 2017; Guo et al., 2019; Melro, Filipe, et al., 2021; Protz, Lehmann, Ganster, & Fink, 2021; Sescousse, Smacchia, & Budtova, 2010). Moreover, cellulose-lignin interactions have been measured using the AFM colloidal probe force technique as a function of aqueous electrolyte solution conditions, with cellulose as the probe against solid kraft lignin thin films (Notley & Norgren, 2006). However, as far as we know, no previous studies have addressed the effect of lignin, as an amphiphilic additive, on cellulose dissolution. In view of its apparent amphiphilic character, lignin is here suggested as a potential sustainable additive to improve cellulose dissolution in aqueous-based cold alkali. Whereas this is the main issue of the present study we also note a broader scope of characterizing the interactions between lignin and cellulose, which includes the development of new materials of superior performance from the lignocellulose biomass. Lignin, when successfully blended with other polymers, offers particularly interesting properties, namely, antioxidant and antimicrobial activities, UV shielding, increase in thermal conductivity and flame retardancy (Melro, Filipe, et al., 2021). The lignin effect on cellulose dissolution was evaluated by turbidimetry, polarized light microscopy (PLM) and dynamic light scattering (DLS). Rheometry was also implemented to access the gelation behavior of the cellulose dopes upon temperature cycles while X-ray diffraction was applied to elucidate the effect of lignin on the molecular organization of the regenerated materials.

2. Materials and methods

2.1. Samples preparation

The cellulose source was microcrystalline cellulose (Avicel PH101, Sigma Aldrich) with a weight-average molecular weight (M_w) of $\approx$ 62,000 g/mol and a polydispersity index of 3.85, as determined by size exclusion chromatography. NaOH (99.2% purity) was purchased from VWR chemicals while urea ($\geq$99% purity) and kraft lignin, with a sulfur content of ca. 4% and a M_w of $\approx$ 10,000 g/mol, were obtained from Sigma Aldrich.

Stock solutions of the NaOH-based solvents (i.e., NaOH and NaOH-lignin aqueous solutions) were prepared in advance. The NaOH concentration range was 5–7 wt% while the lignin concentration was 1–2 wt%. Samples containing 4 wt% urea were used as reference. The cellulose concentration was kept constant in all trials (i.e., 4 wt%). The samples were prepared following an adapted procedure (Pereira et al., 2018). Briefly, the solutions were prepared by adding the cellulose powder to the NaOH-based solvents at room temperature. Then, the cellulose suspensions were stirred in a vortex for 1 min and placed in a freezer at −30 °C. After 10 min cooling, the suspensions were stirred again in the vortex for 1 min and placed back in the freezer. After another 10 min, the

ice slurry suspensions were stirred for 2 min with an Ultra-turrax at 10000 rpm, and left in the freezer overnight (12-16 h). After thawing the samples at room temperature for 2 h, cellulose dissolution was completed (evaluated by the naked eye and light microscopy).

2.2. Turbidimetry

The turbidity of the samples was determined using a Hach RATIO/XR 43900 turbidimeter, equipped with a tungsten lamp. The turbidity readings were performed directly on the instrument, using a nephelometric turbidity unit (NTU) scale, based on white light (400–680 nm) and 90° incident angle. In order to correct for the intrinsic color of the lignin-containing samples, the turbidity of all NaOH-based solvents was measured before making the final cellulose solutions, and subtracted from the turbidity of the final solutions. The measurements were performed with matched Hach glass sample cuvettes with screw caps at 25 °C and 45 °C. Samples were kept at the desired temperature for a certain period, through their immersion in a water-bath, and then removed, cleaned with paper cloth, and placed in the turbidimeter for immediate readings. This procedure was periodically repeated during 2 h at each temperature (25 or 45 °C).

2.3. Rheology

Rheological measurements were carried out with a controlled stress MCR 300 rheometer (Anton Par) equipped with a cone-and-plate geometry (49.95 mm diameter and 1.006° angle). The complex viscosity of the cellulose solutions was followed for 12 h, while stepwise cycling the temperature. More specifically, samples were loaded at 15 °C, and then the temperature was raised to 25 °C. At this stage, the time-resolved dynamic oscillatory measurements started (constant angular frequency of 1 rad/s and strain of 0.1%) and were performed for 12 h, while alternating the temperature between 25 and 45 °C, for every 2 h. The temperature was controlled by a Peltier unit and a suitable solvent trap was used to minimize solvent evaporation.

2.4. Polarized light microscopy

Samples were observed on a Leica DMRX optical microscope. Typically, a small droplet of the dopes was placed on a glass slide and covered with a cover slip. Samples were analyzed by transmitted light polarization using cross polarizers, at 20× magnification. Pictures were captured using Leica DFC 320 camera with 5 megapixels and analyzed with the microscope software (Leica LAS v4.5).

2.5. Dynamic light scattering

The hydrodynamic diameter of the particles in solution was determined using a Malvern Zetasizer Nano ZSP, equipped with a laser of 633 nm wavelength and a 173° backscatter detector (NIBS). Starting solutions of 2 wt% lignin, 4 wt% cellulose and the mixture of both (in 7 wt% NaOH aq. solutions) were progressively diluted with the NaOH solvent until count rates and correlograms met the requirements for a reliable measurement. The total polymer concentration in the three samples was between 0.05 and 0.06 wt% after dilutions. For each sample, three independent measurements were made with an automatic number of runs set by the instrument (typically between 11 and 16). For a multimodal distribution, the peak mean sizes were reported based on the intensity distribution analysis, while the relative proportions of each peak were reported based on the volume distribution analysis. Mie theory is used in the Nano software to convert the intensity distribution into a volume distribution, using the optical parameters of the analytes (Stetefeld, McKenna, & Patel, 2016).

2.6. X-ray diffraction

X–ray diffraction (XRD) was performed at room temperature using a Bruker D2 Phaser diffractometer with Cu Kα radiation (wavelength λ = 1.54 Å) at 30 kV and 10 mA, in θ-2θ geometry. The increment was fixed at 0.02°. The samples were prepared under comparable conditions and were fixed on a silicon single crystal to provide low background interference. All the cellulose dopes, containing 4 wt% cellulose, were poured in identical glassware and first dried in air. The samples were then washed in water until the pH of the waste waters was close to 7; they were dried in air and kept sealed in an airtight box until analyzed. The thickness and solid-dry content of the samples was measured, the values being approximately the same for all samples: 89.6 ± 1.5% solid-dry content and ≈310 ± 10 μm thickness.

3. Results and discussion

The main goal of this work was to evaluate the effect of lignin on cellulose dissolution in cold NaOH (aq.) solutions. This was done by following the changes in the turbidity of the samples when varying solvent composition, time, and temperature. Since the scattering intensity depends on the size and density number of the aggregates (Stetefeld et al., 2016), this is a suitable technique to infer about the dissolution state of macromolecules, as well as aging and temperature effects. Other methods, such as PLM, DLS, rheometry and XRD, can give further insight on the bulk properties of the cellulose-lignin solutions, as well as the subsequent regenerated materials.

3.1. Effect of lignin on cellulose dissolution in NaOH solution

In Fig. 1A, it is possible to observe that the addition of lignin to the alkali cellulose solutions decreases the turbidity of the samples. This effect is even more striking as the NaOH concentration is reduced. Moreover, cellulose aggregation within 48 h storage at room temperature seems to become less pronounced for the samples containing lignin, which is evidenced by the substantial differences in turbidity with respect to the samples without lignin, and especially for the lowest NaOH concentrations (ca. 70 to 260 NTU reduction) (Fig. 1B). The fact that lignin improves cellulose dissolution is supported by PLM. While the samples without lignin appear to be more coarsely structured (larger aggregates or undissolved crystallites), the sample containing lignin looks better dissolved with no perceptible large aggregates (Fig. 1D). The effect of lignin on the average size of cellulose aggregates was also probed by DLS. Data shows that all tested samples were composed of two main size distributions, the second peak suggesting partial colloidal aggregation in solution. Regarding the main peak (Peak 1 in Table 1 and

Table 1
Mean sizes deduced from the DLS peaks and their percentage in volume.

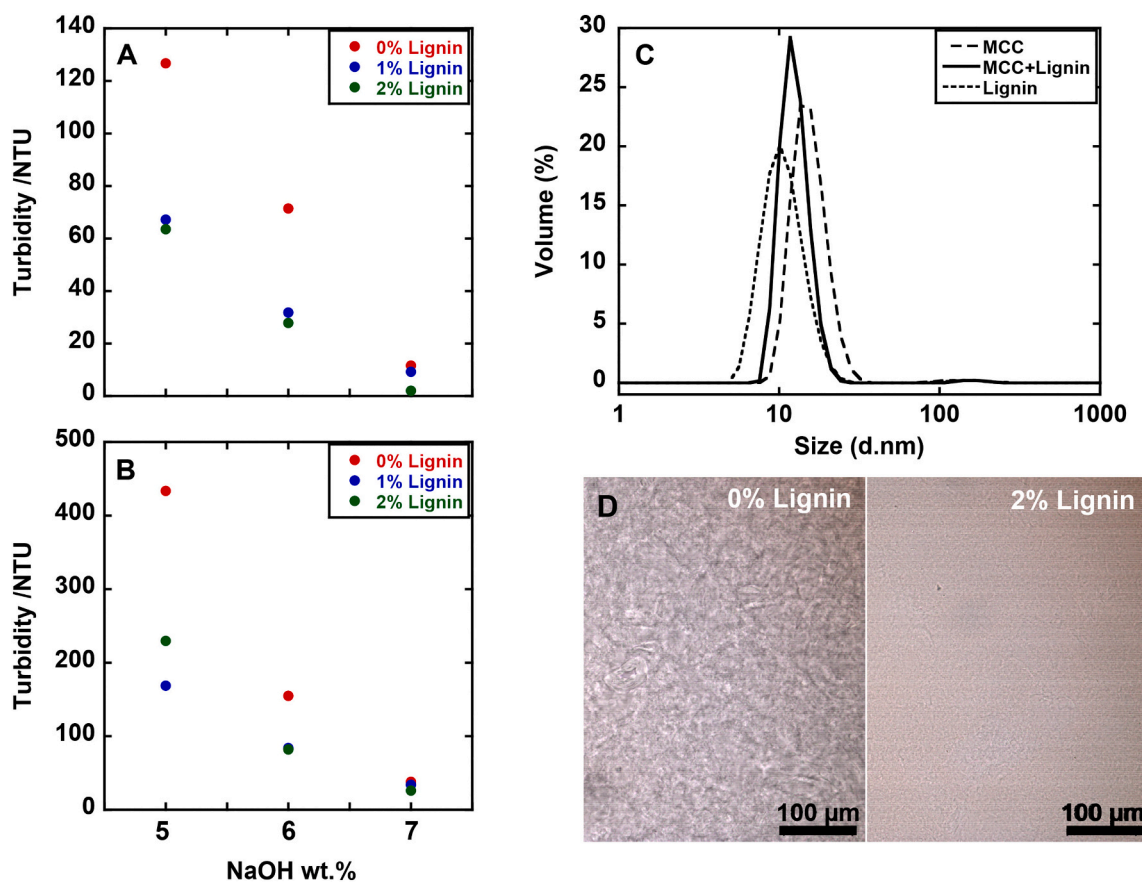| Samples	Peak 1 mean size (d. nm)[a]	Vol %	Peak 2 mean size (d. nm)[a]	Vol %
MCC	17.9 ± 4.0	98.9	141 ± 38	1.1
MCC + Lignin	13.6 ± 2.5	99.3	162 ± 28	0.7
Lignin	12.6 ± 3.7	99.2	167 ± 49	0.8

[a] Determined by intensity distribution analysis.

Fig. 1. Turbidity of 4 wt% cellulose solutions containing lignin concentrations from 0 to 2 wt% in a range of NaOH concentrations of 5–7 wt%, freshly prepared (A) and after 48 h aging (B). C) Size distribution of the freshly prepared NaOH (7 wt%) solutions of cellulose, lignin, and the mixture cellulose/lignin (4 wt% cellulose and 2 wt% lignin). D) Polarized light microscopy images of the aged (48 h) cellulose solutions in 5 wt% NaOH, without the addition of lignin (left image) and with the addition of 2 wt% lignin (right image).

Fig. 1C), it is possible to conclude that lignin is not detrimental to the dissolution process, the sizes being in the same range as for cellulose and lignin alone. These results support the turbidity differences between samples with and without lignin in the best NaOH conditions as discussed above (Fig. 1A).

3.2. Aging of cellulose-lignin solutions

It is well established that cellulose solutions in cold alkali are often metastable and thus sensitive to aging or pH and temperature changes, which may trigger gelation-regeneration of the cellulose dopes (Isobe, Kimura, Wada, & Kuga, 2012; Medronho & Lindman, 2015; Pereira et al., 2018; Roy, Budtova, & Navard, 2003). In order to infer on the aging effect, measurements were made periodically, within 48 h, and at room temperature. As can be observed in Fig. 2, in all three different NaOH conditions, there is a visible effect of lignin in lowering the turbidity of the samples. This effect becomes much more noticeable as the NaOH concentration decreases and for longer aging times. In these conditions, a substantial decrease (ca. 40–50%) in turbidity of the samples containing lignin versus the ones without lignin is observed. These results strongly suggest that lignin may interact with cellulose preventing/delaying its aggregation with time. The differences in having 1 or 2% lignin were more noticeable in the highest NaOH concentration (i.e., 7% NaOH). As the NaOH concentration decreases, the differences become negligible (i.e., 6% NaOH) or are even slightly reversed with the aging of the solutions (i.e., 5% NaOH).

Two main factors controlling the cellulose dissolution in aqueous media have been recently highlighted, namely the elimination or reduction of the hydrophobic interactions between cellulose molecules and cellulose ionization by protonation (in acidic media) or deprotonation (in alkaline media) (Lindman et al., 2017; Lindman et al., 2021; Medronho & Lindman, 2014). We note that in general the effect of alkali concentration in cellulose is nonmonotonic with a maximal effect at intermediate values. This can be referred to a balance between two effects, increasing alkali concentration increases the degree of ionization, and increasing ionic strength decreases repulsion between cellulose molecules. Similarly, lignin dissolution in alkali is also affected by a decisive balance between electrostatic and hydrophobic interactions (Melro et al., 2018; Melro, Valente, et al., 2021). However, it is important to note a principal difference related to the large difference in pKa values of ionizing groups. Due to the difference in pKa values, the role of the counterion is entirely different. Lignin ionizes in a pH range of 9–10 and shows a typical polyelectrolyte behavior in that solubility is controlled by the counterion entropy. This, in turn, is determined by the degree of counterion association. Thus, the solubility is highest for the most polar counterions; this explains why solubility is higher for lithium than for sodium and potassium and significantly reduced with more hydrophobic counterions (Melro et al., 2020). For cellulose, the situation is different since the relevant pH region is 13–14. The dissolution does not depend on whether LiOH, NaOH or KOH are used to obtain a particular pH. A larger amount of KOH is, however, needed to obtain the same pH than for the stronger bases (LiOH and NaOH), since it is slightly less dissociated, i.e., for a certain molar concentration of KOH the concentration of free hydroxide ions is lower and therefore also the pH. A discussion on the differences in pKb values for the alkali metal hydroxides can be found in Bialik et al., which also provides relevant references to the literature (Bialik et al., 2016). Hence, an apparent alkali ion specificity may appear due to the interaction between alkali and hydroxide ions (Alves et al., 2016; Xiong et al., 2013). For cellulose, because of the high pH range and the less important role of counterion entropy, hydrophobic counterions, such as tetrabutylammonium, strongly facilitate dissolution (Alves et al., 2015; Gubitosi, Duarte, Gentile, Olsson, & Medronho, 2016; Medronho et al., 2016). In the same direction, the results of the present study also demonstrate that the addition of lignin can significantly facilitate cellulose dissolution in NaOH solutions by presumably weakening the hydrophobic interactions
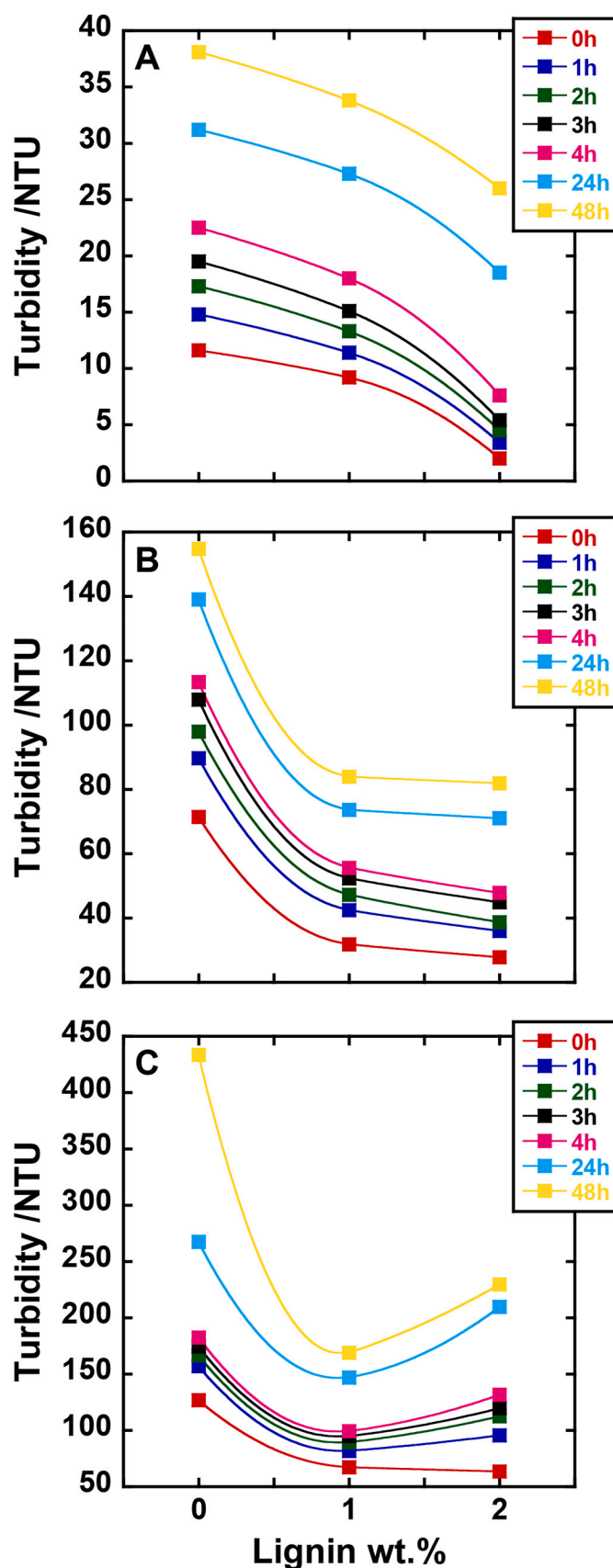

Fig. 2. Turbidity of 4 wt% cellulose solutions containing lignin concentrations from 0 to 2 wt% prepared at (A) 7 wt% NaOH (aq.), (B) 6 wt% NaOH (aq.) and (C) 5 wt% NaOH (aq.) and at different aging periods up to 48 h.

between cellulose molecules (Alves et al., 2016; Medronho et al., 2015; Medronho & Lindman, 2014). Nevertheless, the effect of lignin depends on the NaOH concentration. In understanding why the effect of lignin is complex and different for various NaOH concentrations, we have to consider that lignin is a weak acid. As mentioned above, the phenolic groups of lignin have a lower pK_a value than the hydroxyls of cellulose and, therefore, at a given NaOH concentration, the pH will be lowered due to the presence of lignin; this will consequently lower the ionization degree of cellulose thus limiting its dissolution.

Shi et al. have studied the effect of the lignin content on the dissolution of softwood pulps in NaOH-urea solvent (Shi, Yang, Cai, Kuga, & Matsumoto, 2014). The authors recognized that the behavior is complex and does not follow a linear relationship with the lignin content. In their case, it was observed that when lignin concentration increases from 0.3 to 2.8%, the dissolved amount of pulp increases from 12 to 26%. This beneficial effect of low concentrations of lignin in pulp dissolution supports our findings. Curiously, above 2.8% lignin content, the dissolution of pulp becomes poorer. This weakening of solvent quality, above certain lignin amount, might be related to what has been previously discussed. As the phenolic groups of lignin have a lower pK_a value than the hydroxyls of cellulose, at a given NaOH concentration, the pH will be lowered due to the presence of lignin; this will consequently lower the ionization degree of cellulose thus limiting its dissolution. In the same view, this concentration limit might also be lowered for lower NaOH concentrations, and that is probably why a slightly reversed behavior was observed when increasing lignin concentration in the 5% NaOH solvent (Fig. 2C).

3.3. Comparison between lignin and urea in cellulose dissolution

Urea has a lower polarity than water and is well known to eliminate hydrophobic association in water (Zangi, Zhou, & Berne, 2009). For instance, it acts as a protein denaturant by reducing intramolecular hydrophobic association and also inhibits hydrophobic association of surfactants and block copolymer as can be seen from the increase in the critical micelle concentration upon urea addition (Lindman et al., 2021). Urea is also a well-known additive in cellulose dissolution in alkali media (Budtova & Navard, 2016; Cai & Zhang, 2005). By comparing the behavior of cellulose solutions prepared in NaOH-urea with those in NaOH-lignin aqueous solutions, the role of lignin in cellulose dissolution can be addressed. In Fig. 3, three alkali solvents, neat NaOH, NaOH-

urea, and NaOH-lignin, were compared regarding their effects on cellulose dissolution. As it can be observed, lignin shows a rather similar effect on cellulose solutions turbidity as urea. Both additives are capable of decreasing the turbidity of the solutions, and hence, enhancing the solvent quality. It is noted that in the poorer NaOH conditions, lignin seems to be more efficient in promoting cellulose dissolution than urea, with an improved stability with aging of the solutions (Fig. 3A). On the other hand, for higher NaOH concentrations, urea performs better than lignin and this might be related to the weakly acidic nature of lignin and its ionization dependence of pH, as discussed above (Fig. 3B).

3.4. Gelation kinetics with temperature

As mentioned above, cellulose solutions (particularly when dissolved in alkali-based systems) are typically metastable. Temperature strongly influences the gelation kinetics of cellulose-NaOH (aq.) solutions (Pereira et al., 2018; Roy et al., 2003). Temperature also affects lignin solution stability, but the effect is not significant at alkalinities above 4 wt % and temperatures below 100 °C (Norgren, Edlund, Wågberg, Lindström, & Annergren, 2001; Norgren & Lindström, 2000). In Fig. 4, time-resolved turbidity and viscosity assays were performed on samples with and without lignin, where the temperature was alternating between 25 and 45 °C for 12 h. As it can be seen, the turbidity remains essentially constant when the temperature is 25 °C, while it increases with time at 45 °C. This shows that at 45 °C there is a gradual increase in cellulose aggregation, but such increase is not observed at 25 °C. The fact that the turbidity and the complex viscosity are retained when lowering the temperature from 45 to 25 °C indicates that the aggregation is irreversible and that at 25 °C, the solutions are only kinetically stable, in agreement with previous works (Pereira et al., 2018; Roy et al., 2003). This phenomenon seems to be independent of lignin presence or not, but a clear decrease in the viscosity on the sample containing lignin was noticeable during the whole experiment; the viscosity is less than 350 Pa•s at the end of the experiment (12*h*) in comparison to the neat NaOH (aq.) solvent. This suggests that the gel network formed was weaker than that of the sample not containing lignin, meaning that aggregation of cellulose and 3D network became less effective in the presence of lignin. This was also confirmed from the turbidity experiments; aggregation was much weaker in the sample containing lignin, evidenced by a decrease in turbidity of more than 300 NTU compared to the sample not containing lignin (Fig. 4B). Although the presence of
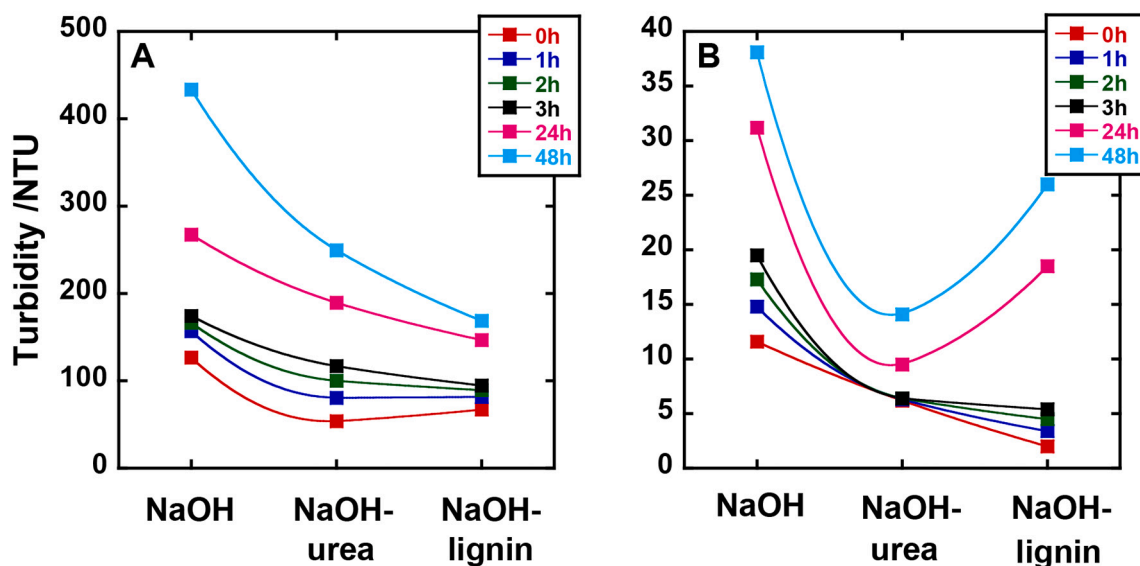

Fig. 3. Turbidity at different aging periods of 4 wt% cellulose solutions dissolved in neat NaOH (aq.), NaOH-urea and NaOH-lignin. For each NaOH concentration, the lignin concentration was chosen based on its best efficiency in that specific concentration; 1 wt% lignin in graph A (5 wt% NaOH) and 2 wt% lignin in graph B (7 wt% NaOH). Urea concentration used was 4 wt% in both cases.
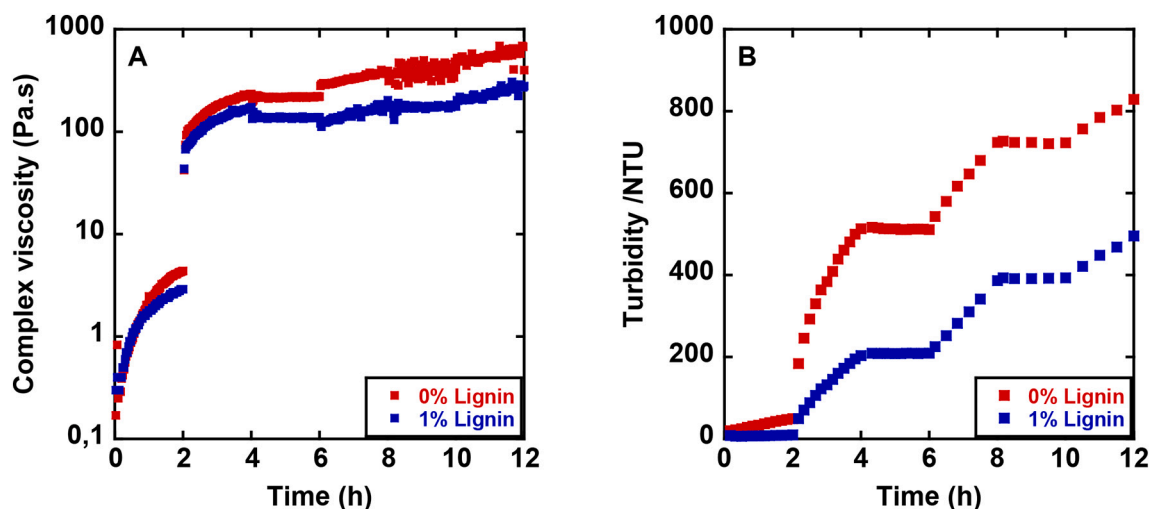
Fig. 4. Complex viscosity (A) and turbidity (B) of cellulose solutions without lignin (red squares) and with 1 wt% lignin (blue squares) in 7 wt% NaOH (aq.). The temperature was alternating between 25 and 45 °C, for every 2 h, starting with 25 °C in the first 2 h.

lignin in 7 wt% NaOH (fresh and aged samples, Fig. 2A) did not reveal such a dramatic effect on the turbidity of the samples as for the lowest NaOH concentrations, lignin is seen to substantially improve the gelation kinetics of the cellulose solution upon heating. Our results, performed with kraft lignin, seem to contrast with the results obtained by Sescousse et al. with organosolv lignin in neat 8 wt% NaOH aqueous solutions. In their study, the gelation time of microcrystalline cellulose dopes decreases while adding small amounts of lignin (1–2%), and they suggest that the electrostatic repulsion between the polymers is possibly leading to a micro-phase separation of the two polymers, creating lignin-rich and cellulose-rich domains, and thus, accelerating gelation (Sescousse et al., 2010). These findings appeal for further investigations on the influence of different types of lignins in cellulose dissolution and regeneration.

3.5. Effect of lignin on regenerated cellulose

So far, the role of lignin has been evaluated regarding its effect on the dissolution of cellulose. It is reasonable to assume that the solution state of cellulose dopes, together with the micro-morphology structural features induced by the regenerating/processing methods, have a considerable impact on the properties of regenerated materials. This is striking, for instance, regarding the features of cellulose-based films and fibers (Budtova & Navard, 2016; Jiang et al., 2012; Yang, Qin, & Zhang, 2011; Zhang, Ruan, & Gao, 2002). Therefore, cellulose was regenerated from the different alkali solvents and evaluated by XRD assays. The solid-state features of the regenerated materials depend on many variables playing during regeneration and drying steps, and therefore establishing a simple cause-effect relation with the dissolved state is not straightforward. However, it is known from the literature that the crystallinity of cellulose II is affected by the presence of additives that are able to weaken the hydrophobic interactions. In that regard, our goal with this analysis was to infer about those crystallinity changes, by comparing the diffractograms of regenerated cellulose samples from neat NaOH, NaOH-urea and NaOH-lignin aqueous solutions. As shown in Fig. 5, the diffractogram peaks for all the regenerated cellulose samples are identical to the ones found for the cellulose II polymorph. These peaks are located at the diffraction angles (2θ) 12.6°, 20.6°, 22.1°, and 34.8°; corresponding to the crystallographic plane reflections (1−10), (110), (020), and (004), respectively (From et al., 2020; Nam et al., 2016). Similar to what is observed for the neat NaOH (aq.) and NaOH-urea (aq.) systems, a transition from cellulose I to cellulose II polymorph is also observed upon the regeneration of the sample prepared with the NaOH-lignin solvent system. Cellulose II polymorph crystallizes as monoclinic
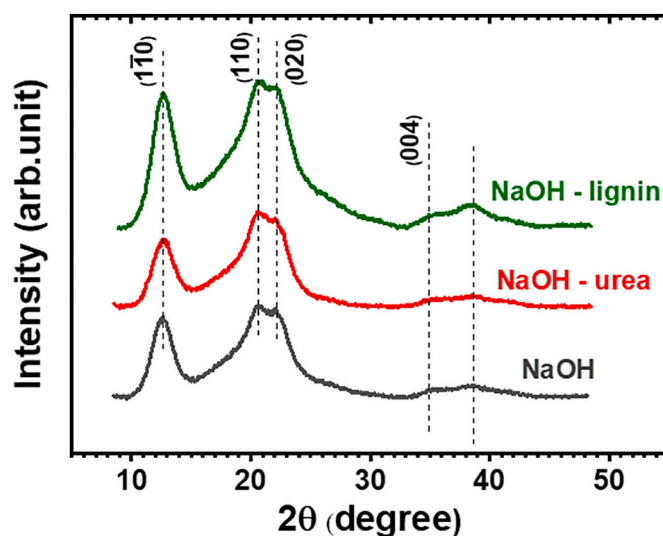

Fig. 5. X-ray diffraction (XRD): profiles of cellulose regenerated samples prepared from various NaOH-based solvents (e.g. NaOH, NaOH-urea and NaOH-lignin aqueous solutions). The positions of expected Bragg peaks from the cellulose II polymorph are marked and labelled with their respective Miller indices (Nam, French, Condon, & Concha, 2016).

Table 2
Crystallinity indices and crystallite sizes of the different regenerated cellulose materials from the various NaOH-based solvents. The XRD data on (1–10) crystallographic plane was used for the calculations.

Solvents	Crystallinity index (%)	Crystallite size (nm)
NaOH	72.3	3.99
NaOH-urea	70.4	3.89
NaOH-lignin	66.8	3.52

crystals with the unit cell containing two individual chains arranged in an antiparallel fashion (Hori & Wada, 2006; Langan, Nishiyama, & Chanzy, 2001; Langan, Sukumar, Nishiyama, & Chanzy, 2005). For all solvent systems, the lattice d-spacing and unit cell parameters were calculated and presented in Table S1 and S2 of the *supplementary material*; crystallinity indices and crystallite size were estimated and are presented in Table 2.

Detailed information on the calculations and data analysis is given in the *supplementary material* file. The d-spacings and unit cell parameters of cellulose II were found to remain unchanged in all NaOH-based systems. All the calculated parameters closely matched the values reported in the literature for cellulose II polymorph (Hori & Wada, 2006; Langan et al., 2001; Langan et al., 2005). On the other hand, the crystallinity indices and crystallite sizes of the regenerated cellulose II were found to decrease in the following order NaOH > NaOH-urea > NaOH-lignin. The preliminary data suggests that lignin disturbs the packing of the cellulose molecules, interfering with the crystalline structure of cellulose. Due to the manifest amphiphilic features of lignin discussed above, we would expect it to weaken hydrophobic interactions similarly to urea, resulting in a less crystalline regenerated material (Alves et al., 2016). Moreover, the slight reduction in crystallite size of the regenerated cellulose material provides additional support to the PLM images (Fig. 1C), where a reduction in the structured networks of aged cellulose-lignin samples was also observed.

4. Conclusions

In this work, lignin was evaluated as a potential renewable and green additive for enhancing cellulose dissolution in cold alkali. Lignin was observed to not only improve cellulose dissolution but also delay the gelation kinetics upon aging or temperature increase of the solutions. Data supports the hypothesis of lignin acting as a beneficial amphiphilic additive, weakening the hydrophobic interactions among the crystalline planes of cellulose. Regenerated materials from cellulose-lignin solutions also revealed lower crystallinity as reported in the literature for other superior aqueous solvents, such as NaOH-thiourea and aqueous tetrabutylammonium hydroxide (TBAH). With this novel approach, it is possible to use a renewable resource and plenty available to extend the dissolution window of the cold alkali track to lower NaOH concentrations (e.g., 5 wt% NaOH), making this solvent system more appealing and sustainable.

CRediT authorship contribution statement

Carolina Costa: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Bruno Medronho:** Conceptualization, Writing – review & editing, Supervision. **Alireza Eivazi:** Investigation, Writing – review & editing. **Ida Svanedal:** Investigation, Writing – review & editing. **Björn Lindman:** Writing – review & editing, Supervision. **Håkan Edlund:** Conceptualization, Writing – review & editing. **Magnus Norgren:** Conceptualization, Writing – review & editing, Supervision.

Declaration of competing interest

None.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbpol.2021.118661.

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