Deep Eutectic Solvent Delignification to Low-energy Mechanical Pulp to Produce Papermaking Fibers

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A novel process based on low-energy mechanical pulp and deep eutectic solvents (DESs) was evaluated with the goal of producing fibers suitable for papermaking. Ideally, these fibers could be produced at much lower costs, especially when applied to an existing paper mill equipped with a thermomechanical pulp (TMP) production line that was threatened with shutdown due to the decreasing demand for wood-containing paper grades. The efficiency of DES delignification in Teflon-coated autoclaves and in a specially designed non-standard flow extractor was evaluated. All tested DESs had choline chloride ([Ch]Cl) as the hydrogen bond acceptor. Lactic acid, oxalic acid, malic acid, or urea acted as hydrogen bond donors. The temperatures and times of the delignification tests were varied. Chemical analysis of the pulp samples revealed that DESs containing lactic acid, oxalic acid, or urea decreased the lignin content by approximately 50%. The DES delignification based on [Ch]Cl and urea exhibited good hemicellulose retention while DES systems based on organic acids resulted in varying hemicellulose losses. The [Ch]Cl / urea mixture did not appear to be corrosive to stainless steel, which was another advantage of this DES system.

Keywords: Asplund pulp; Deep eutectic solvent; Delignification; Tensile strength; Thermomechanical pulp

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INTRODUCTION

The greatest threat to the future of mechanical pulp is its high specific energy consumption (Sixta 2006). Paper mills with thermomechanical pulp (TMP) processes are greatly affected due to their considerably high energy demand. Moreover, with the constant need to improve the profitability of wood-containing paper grades, such as newsprint and magazine, TMP mills need to find ways to reduce their operational costs. Despite many research efforts to develop a novel mechanical pulping process that is more energy-efficient than the traditional mechanical pulping processes, there is still a substantial need for improvement. Therefore, more drastic measures and even completely new innovations are needed. One novel idea is to utilize an existing TMP process as a pre-treatment for a novel direct-dissolving chemical fractionation, such as that based on deep eutectic solvents. In this process concept, the energy consumption in the TMP pre-treatment must be substantially lower than that in the conventional TMP process, to prevent the new process from becoming economically unfeasible (Hendriks and Zeeman 2009). Moreover, in the course of combined mechanical and chemical treatments, the fibers could be engineered in such a way that it creates a completely new type of pulp.

Deep eutectic solvents (DESs) are ionic solvents that are typically composed of an organic salt and at least one hydrogen bond donor (Fig. 1); the combination presents a lower melting point than any of its individual components (Abbott *et al*. 2004). The formation of a liquid mixture at room temperature is due to the formation of hydrogen bonds between a hydrogen bond donor (HBD), and a hydrogen bond acceptor (HBA). DESs contain large, asymmetric ions that have low lattice energy, which explains their low melting points (Smith *et al*. 2014). The research into DESs is relatively novel, with the first scientific paper on the subject published as late as 2001 (Abbott *et al*. 2001; Pena-Pereira and Namieśnik 2014). DESs are nature-based, renewable, biodegradable, low-volatile, and cost-effective. Currently, numerous DES applications in various fields of chemistry and chemical engineering are being studied. One rapidly growing area of DES research is the use of DES in biomass fractionation (Van Osch *et al*. 2013), because DESs are sustainable yet inexpensive alternatives to much more cumbersome solvents that have been suggested for fractionating wood or other types of biomass.

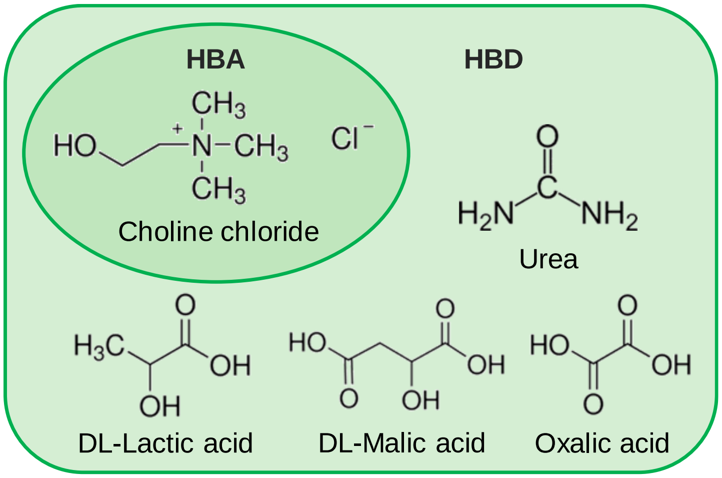

Fig. 1. Chemical structures of the DESs investigated in this research, using choline chloride as the hydrogen bond acceptor (HBA); HBD: hydrogen bond donor

The extent to which lignin interacts with DES is proportional to the exposed surface area of the lignocellulosic biomass, as well as its lignin content. The rigid and compact structure of the plant cell wall makes lignocellulosic material, such as wood, very resistant against chemical degradation (Zhao *et al*. 2012). This natural resisting power of the fibers is a technical obstacle for its treatment with direct-dissolving solvents such as DESs. It has been shown previously that wood is simply not soluble in non-derivatizing direct-dissolution solvents without a chemical or mechanical pre-treatment (Kyllönen *et al*. 2013; Deb *et al*. 2016). One effective way to facilitate the distribution of chemicals and their penetration into wood is to decrease the size of the wood particles. The main objective is to have a large surface area, which in turn leads to high reaction rates with DESs. This can be achieved by mechanically fiberizing wood prior to DES treatment. It is well-known that fiberizing wood chips at standard conditions for TMP to obtain good strength properties and low shives content requires a substantial energy consumption. At higher temperatures (exceeding 150 °C), the fibers are mainly separated in the middle lamella due to thermal softening of the lignin, resulting in more intact fibers of very low bonding, and are covered by a lignin-rich layer. In such pressurized refiners, of which the Asplund defibrator is the prototype (Suchsland and Woodson 1987), the chemical changes in the wood constituents alter fibers to be less reactive to pulping chemicals, but the specific energy consumption and fiber damage decrease (Rydholm 1965). By subjecting the biomass (in the form of wood chips) to a low-energy mechanical treatment, its accessible surface area increases substantially without compromising its chemical composition, which in turn ensures sufficient product quality and yield. Delignification tests using two types of mechanical pulp and DESs have been reported previously (Choi *et al*. 2016a,b). However, as for the knowledge of the authors of this manuscript, there have been no research publications generally available regarding the use of low-energy mechanical pulp (Asplund fibers) as starting material for DES pulping.

EXPERIMENTAL

Materials

Asplund fibers are Norway spruce (*Picea abies*) fibers produced by mechanical defibration of spruce chips after preheating to a temperature above the softening temperature of lignin (approximately 180 °C is common) in a pressurized refiner at the same temperature. The product is a high-yield mechanical pulp of markedly unbroken fibers (Asplund 1953). The energy input for the Asplund defibration is usually in the range of 200 kWh/ton. However, the authors assumed that even lower specific energy could produce fibers with sufficiently good separation. In this research, a high shives content is acceptable because the main objective was to have a large surface area. Asplund fibers were manufactured with a specific energy of 120 kWh/ton at a pilot plant at Valmet AB (Sundsvall, Sweden). The initial tests were carried out with the Asplund pulp “as is”, *i.e.*, without screening. Later in this research, the Asplund pulp underwent a screening to remove shives (also at Valmet AB, Sundsvall, Sweden). The pulp contained approximately 95% of dry solids before the laboratory experiments.

The flow extraction, two-stage delignification, and PFI refining (Papirindustriens Forskningsinstitutt – the Norwegian Pulp and Paper Research Institute) were conducted at MoRe Research (Örnsköldsvik, Sweden). The unscreened pulp samples were subjected to five different refining levels and the screened pulp samples to three different refining levels in a PFI refiner (PFI A/S, Løten, Norway). Standardized handsheets were prepared using a Rapid-Köthen sheet forming machine (PTI GmbH, Vorchdorf, Austria).

Choline chloride, urea, lactic acid, malic acid, and oxalic acid were purchased from Merck (Darmstadt, Germany) and used as supplied. A molar ratio of 1:2 gives the lowest melting point for [Ch]Cl:Urea (Abbott *et al*. 2003). The molar ratio of 1:2 was also applied for the other DES systems: [Ch]Cl:lactic acid, [Ch]Cl:malic acid, and [Ch]Cl:oxalic acid.

Methods

Initially, small-scale tests in tubes with a stirring magnet and an oil bath for heating were performed to find suitable mixing ratios, as well as reaction temperatures and time of the DES used in this study. The flow extractor made of stainless steel could only be used for the [Ch]Cl and urea DES mixture. The testing of DESs containing organic acids was performed using Teflon-coated autoclaves.

Unscreened fibers (high shive content) were treated with DES based on choline chloride and urea, and the tests were performed for 6 h at 80 °C and 100 °C. For the screened fibers, three different levels of temperatures (60 °C, 80 °C, and 100 °C) and three different reaction times (3 h, 6 h, and 15 h) were applied for the autoclave tests.

Lignin content was determined according to the standard TAPPI T222 om-11 (2011), and hemicellulose and cellulose content were determined according Scan-CM 71:09 (2009). Tensile testing was performed according ISO 1924-3 (2005). Pulp and fibers were characterized for their shives content with PulpEye® (Örnskoldsvik, Sweden). Fiber length was determined according ISO 16065-2 (2014).

RESULTS AND DISCUSSION

The shives content of the Asplund pulp was high and may have been even higher if a mill refiner had been used. The screened fibers were treated with DES based on [Ch]Cl and urea at three different temperatures (60 °C, 80 °C, and 100 °C) and at three different reaction times (3 h, 6 h, and 15 h). The Klason lignin content of the fibers was determined before and after DES treatments (Fig. 2).

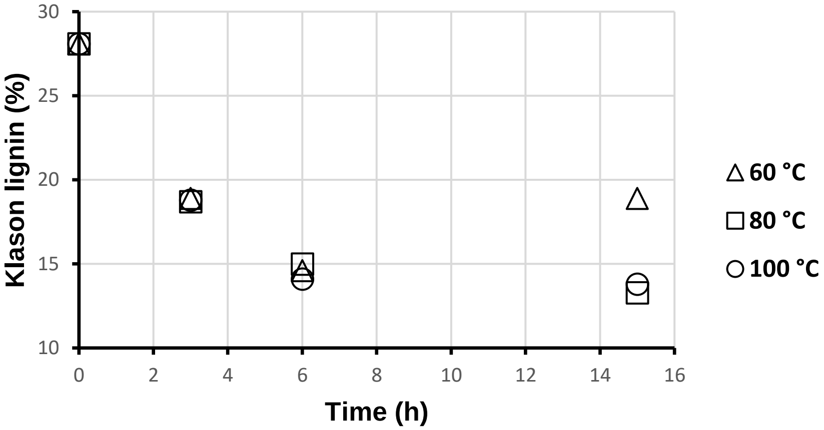

Fig. 2. Pulp lignin content (Klason) at varied reaction times and delignification temperatures

The Klason lignin analysis showed a large reduction of lignin after treatment of 3 and 6 h. However, after 15 h, the sample treated at 60 °C resulted in a higher lignin content compared to 6 h, which might have been due to precipitation of dissolved lignin. For the other two samples, the additional reduction was marginal compared to 6 h. The authors decided to use the conditions that resulted in a lower lignin content during a relatively short time (6 h at 80 °C) for additional experiments. The assumption was that the extraction liquid became saturated after 6 h, which inhibited further delignification. One test was therefore performed in two stages (both for 6 h at 80 °C) with a washing stage between the DES treatments. Another approach included a ‘tailor-made’ flow extractor, which allows liquid to continuously flow around the fibers, presumably improving the delignification. The chemical composition of the untreated pulp and the pulp delignified under various conditions using [Ch]Cl and urea at 6 h and 80 °C for both unscreened and screened fibers is shown in Fig. 3.

The results for unscreened and screened fibers in the one-stage delignification were similar and showed that the removal of lignin was not improved by removing the shives by screening. Compared to the one-stage delignification, the use of either two-stage delignification or the flow extractor did not result in a lower lignin content, but rather the opposite (Fig. 3). This indicated that the construction of the flow extractor needs certain modifications to become more effective. Due to the puzzling results from the two-stage delignification, the experiment was repeated, but the outcome was the same (data not shown). This indicated that after the first stage of delignification, it did not seem to be possible to delignify the pulp further with an additional delignification stage using the same process equipment and fresh DES with the same chemical formulation.

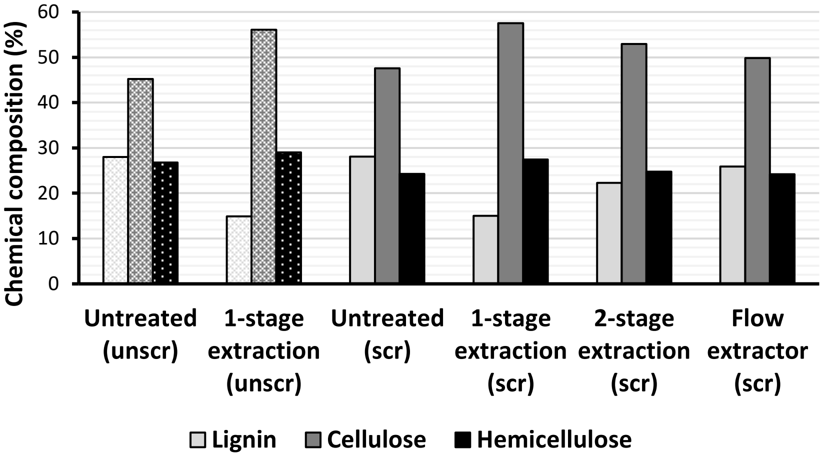

Fig. 3. Chemical composition of the fiber material before and after the delignification with [Ch]Cl and urea for 6 h at 80 °C; bars with the dotted pattern represent unscreened fibers (unscr) while the filled bars denote screened (scr) fibers

The chemical analysis of pulp treated with DES systems based on choline chloride and urea or organic acids (oxalic acid, lactic acid, or malic acid) as HBD in Teflon-coated autoclaves for 6 h at 80 °C is presented in Fig. 4.

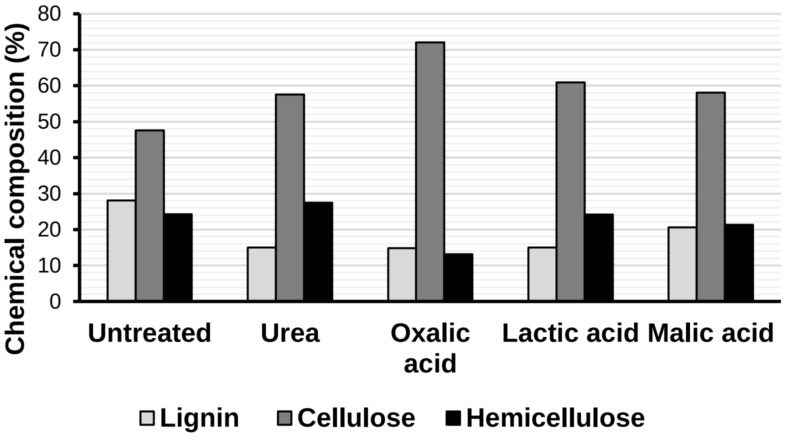

Fig. 4. Chemical composition of the fiber material before and after delignification for 6 h at 80 °C with various DESs

It is worth mentioning that in a pulp delignification study (Smink *et al*. 2019), the application of pure lactic acid resulted in the same conversion compared to a mixture of choline chlorine and lactic acid, although the addition of choline chloride caused a remarkable increase in the delignification rate. In this study, the DESs containing organic acids were able to reduce the lignin content, but they also degraded hemicelluloses to various levels, probably due to increased acid hydrolysis of the hemicellulose (Fig. 4). From all tested DES systems, the mixture of choline chloride and oxalic acid removed most of the lignin and hemicellulose, resulting in the highest ratio between cellulose and lignin. At the same time, the hemicellulose content was the lowest of all tested DES systems. Jablonský *et al*. (2015) delignified wheat straw with DESs based on choline chloride and different organic acids, and observed that the DES containing oxalic acid removed more lignin compared to the other DES systems. In this study, DES treatment by choline chloride and urea resulted in pulp with a remarkably reduced lignin content, while maintaining a high hemicellulose content. Moreover, all tested DESs containing organic acids resulted in apparent corrosion on stainless steel equipment at elevated temperatures, which is why all additional tests were conducted with the DES mixture of choline chloride and urea.

Handsheets were prepared from pulp samples that had been treated with the DES mixture of choline chloride and urea under various conditions. The tensile index results of the tested handsheets are shown in Fig. 5a, and the shive contents, according to PulpEye® measurements, are presented in Fig. 5b.

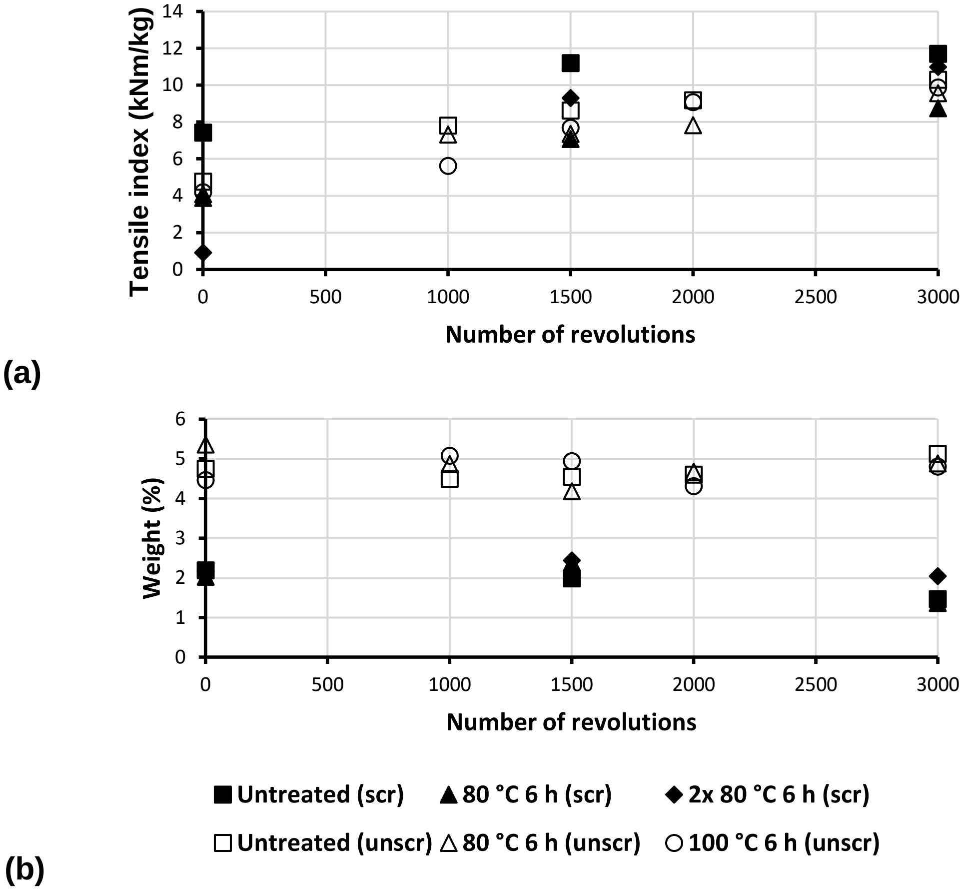

Fig. 5. Tensile index (a) and shive content (b) for DES treatments (choline chloride and urea) at various conditions with both screened pulp (scr) (filled symbol) and unscreened pulp (unscr) (unfilled symbol); number of revolutions indicate the level of PFI mill refining

The unscreened pulp samples were subjected to five different refining levels and the screened pulp samples to three different refining levels. The untreated pulp appeared to have an equal or higher tensile index compared to the treated pulp at all levels of PFI refining. The latter applied for both screened and unscreened pulp (Fig. 5a). In other words, the decreased lignin content in the treated samples did not improve the tensile index.

Screening of the pulp reduced the shives content, although a substantial part remained in the screened pulp (Fig. 5b). DES treatments at various temperatures had no obvious effect on the amount of shives.

Pulp samples that were used for handsheets were also subjected to measurements of fiber length (Fig. 6a) and fiber width (Fig. 6b). Before PFI refining, the length-weighted fiber lengths ranged between 1.7 and 2.1 mm, and these values are almost identical to results published elsewhere for spruce TMP (Sundstrom *et al*. 1993).

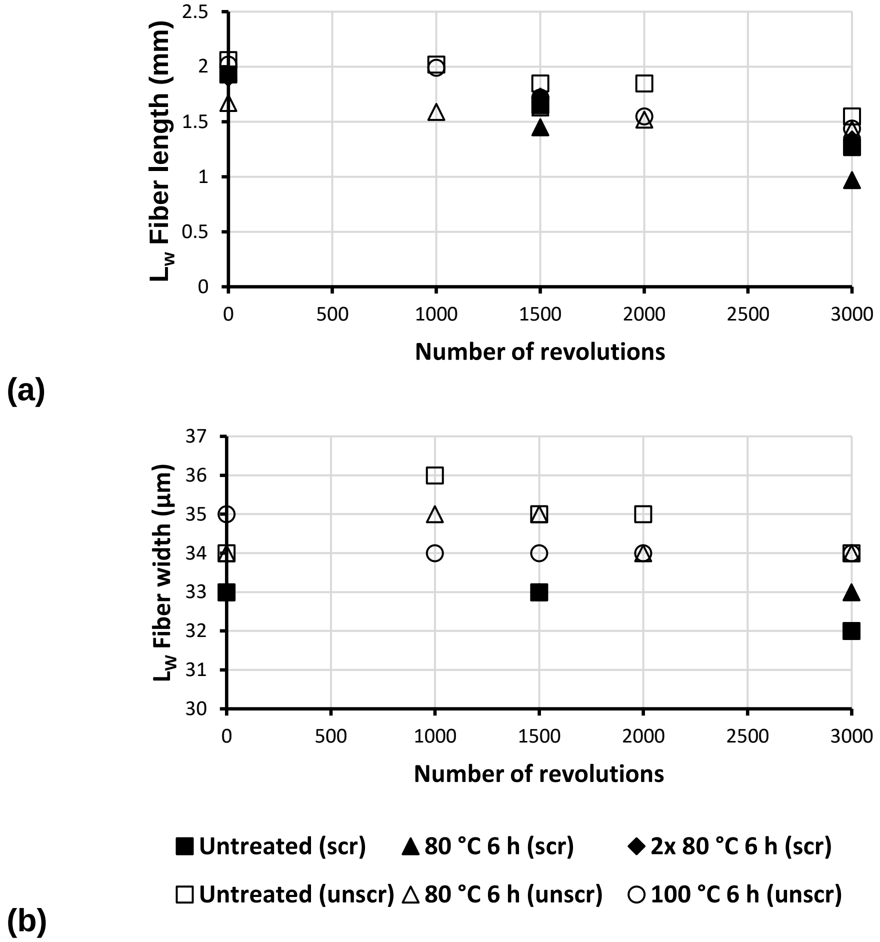

Fig. 6. Fiber length (a) and width (b) before and after DES treatments ([Ch]Cl:urea) at various conditions for screened pulp (scr, filled symbol) and unscreened pulp (unscr, empty symbols); L_W: length-weighted, number of revolutions indicate the level of PFI mill refining

The length-weighted fiber length showed a decrease depending on the amount of revolutions of the mill (Fig. 6a). At all PFI refining levels, the untreated and unscreened pulp sample showed the highest length-weighted fiber length. The pulp that underwent the mildest treatment (80 °C at 6 h) showed the greatest reduction in fiber length.

No clear trend was observed between fiber width and the number of revolutions (Fig. 6b). In general, the differences between the measured fiber widths were rather small. Only for the unscreened pulp, DES treatment appeared to have reduced the fiber width slightly at 1000, 1500, and 2000 revolutions.

Corrosion in the pilot equipment occurred during some of the DES delignification experiments. The corrosion phenomena were investigated with different steel qualities by exposing them to the same DES mixtures at increased temperatures. Under certain conditions, the color of the solvent changed to green due to the dissolution of the steel (Fig. 7). The experiments with the pilot equipment (a non-standard flow extractor) with acidic DESs obviously resulted in corrosion problems at elevated temperatures. To continue this research, only Teflon-coated autoclaves can be used. Alternatively, all stainless steel parts that are in contact with solvents must be exchanged to parts made of titanium.

Fig. 7. Example of corrosion on steel after exposure to acidic DES at 105 °C for 20 h; the green color is due to metal ion dissolution in the DES; the steel quality was standard Cr-Ni-Mo austenitic stainless steel EN 1.4404

Recently, many studies have concentrated on the use of DESs for metal dissolution. Abbott *et al.* (2006) demonstrated successful electro polishing (controlled corrosion of a metal surface) of stainless steel in a [Ch]Cl : ethylene glycol mixture. According to another study of solvatochromic parameters of various DESs (Teles *et al*. 2017), DESs composed of ammonium-based salts and carboxylic acids present a higher capacity to donate and accept protons when compared to most of the other types of direct-dissolution solvents. The latter suggests not only their effectivity in causing corrosion, but also their effectiveness as a direct-dissolution solvent in biomass fractionation.

CONCLUSIONS

1. In this research, for the first time, the delignification of low-energy mechanical pulp with four different deep eutectic solvent (DES) systems was investigated, and it was demonstrated that DES mixtures could reduce the lignin content by almost 50%.
2. Reduction of the lignin content did not improve the tensile strength of the pulp; instead, a minor decrease in tensile index was observed.
3. When lactic acid, oxalic acid, or urea functioned as hydrogen bond donors (HBDs), the delignification was approximately equally effective. When malic acid functioned as a HBD, the DES system was less effective in delignification.
4. The mixture of [Ch]Cl and urea exhibited the best hemicellulose retention of the four tested DES systems in this research. However, to meet the desired quality for

papermaking pulp, delignification must be more effective, and an increase in tensile strength is essential.

5. The presence of carboxylic acids in the DES mixture apparently caused corrosion on stainless steel. No such corrosion was observed after tests with the [Ch]Cl and urea DES mixture.

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