



# Influence of pulping conditions on the pulp yield and fiber properties for pulping of spruce chips by deep eutectic solvent

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Received: 18 September 2023 / Revised: 15 November 2023 / Accepted: 16 November 2023  
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## Abstract

The chemical pulping of wood chips using deep eutectic solvents (DES-pulping) has emerged as an alternative technology to conventional pulping in the paper industry, allowing the production of pulp in combination with the recovery of lignin and sugars for valorization. A challenge in the development of this technology is the understanding of how the operating conditions influence the crucial pulp manufacturing parameters such as delignification percentage, pulp yield, and fiber quality. This work is focused on investigating the effect of operating conditions such as cooking temperature, cooking time, liquor-to-wood ratio, initial water content on DES, type of mixing, the addition of a pre-treatment step (pre-impregnation of DES into the wood chips) to cooking process, and DES composition (lactic acid:choline chloride, lactic acid:sodium chloride, and lactic acid:sodium bromide) on the cooking of wood chips by DES. A shortcut quality evaluation parameter ( $Q$ ), defined as the product of the fiber length and the degree of delignification quantified the quality of the pulping process in a single value, shows values similar to a reference unbleached kraft pulp for cooking at 130 °C in a range of cooking times from 3 to 4.5 h at a L/W of 10:1 by using lactic acid:choline chloride DES. More elaborate property analysis on the fibers showed that several of the the quality-indicating properties of the fibers (coarseness, shape factor, fibril area, and crill index) are comparable with typical sulfite pulping fibers.

**Keywords** DES · Spruce chips · Delignification · Fiber length · Lactic acid · Choline chloride

## 1 Introduction

Kraft pulping is the most widely used method for producing wood pulp for papermaking on an industrial scale. In this process, the wood chips are cooked at high pressure and temperature in a solution called white liquor, comprised of sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S), which causes the lignin and the hemicellulose to depolymerize and dissolve, so that it can be separated from the cellulose fibers [1, 2]. The resulting pulp comprised mainly of cellulose is

then washed and screened to remove the black liquor (the liquor after cooking that contains solubilized and depolymerized lignin and hemicellulose). The pulp is then used to make a variety of paper products, such as office paper [1–3]. The main advantage of the kraft pulping process is its ability to produce strong, high-quality pulp from a wide variety of wood species. However, it also has some disadvantages, such as that lignin is not obtained as byproduct, but burned in the recovery boiler, and the high energy requirements of the pulping process [2, 4]. While the energy is supplied by burning the lignin, and in itself this is a highly integrated process, alternative options that yield more products at low emissions would be desired.

Sulfite pulping is another industrial-scale process that uses solutions of sulfite and bisulfite ions to dissolve lignin and produce cellulose fibers from wood. This process is also used to make high quality paper products (high brightness with smooth surface and resistant to wear and tear). Compared to kraft pulping, sulfite pulping has the advantage of producing paper with better color and printability, as well as a higher cellulose yield, while the fiber strength is

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a bit lower. However, sulfite pulping is more expensive and requires more energy and wastewater treatment than kraft pulping [3].

These factors have led to increased interest in alternative pulping methods that are environmentally friendly and energy efficient. These include soda pulping and organosolv pulping, each with its own advantages and disadvantages. Soda pulping uses sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) instead of sodium hydroxide ( $\text{NaOH}$ ) and sodium sulfide ( $\text{Na}_2\text{S}$ ), which is used in kraft pulping to depolymerize the lignin in wood chips. Although soda pulping has a lower environmental impact than kraft pulping, the resulting pulp may be weaker. Organosolv pulping uses organic solvents such as ethanol or methanol to break down the lignin in the wood chips. While some authors have reported this process to produce a similar quality pulp with a less  $\text{CO}_2$  emissions compared to kraft pulping, it is currently more expensive and energy intensive [1, 3].

Current research is also being conducted on biorefinery approaches, enzymatic and mechanical pulping, and ionic liquid (IL) delignification [2, 5–9]. Biorefinery approaches focus on the efficient conversion of lignocellulosic biomass into a range of bio-based products [10, 11], while enzymatic and mechanical pulping aim to reduce the use of chemicals in the pulping process [1, 2, 4–6, 12].

Cooking of wood chips with deep eutectic solvents (DESs) have been investigated as a potential pulping method alternative to conventional methods that often rely on harsh chemicals and high energy input [13–17]. DESs are composite solvents comprised by hydrogen bond donors and acceptors [15, 18] to form a mixture that shows melting at much lower temperature than would be expected at ideal behavior, for example  $> 50$  °C lower [19], alternatively people do consider the pure component melting points to express that DESs have a pronounced melting point depression as compared to the pure components that make up the DES [15, 18, 20]. Many DESs show low toxicity, biodegradability, and a relatively low cost, making them attractive alternatives to conventional and non/conventional organic solvents (e.g., ionic liquids). The cooking of wood with DES not only allows the delignification of the wood, preserving to a certain extent the cellulose fiber characteristics, but also allows the application of a biorefinery approach by valorizing the dissolved lignin and hemicellulose polymers in the DES-dark liquor (DES after cooking) [15, 17, 18, 21–23].

Several studies have investigated the use of DESs for delignification of wood. Formic acid:benzyltriethylammonium chloride [13], lactic acid:choline chloride [14, 15, 24, 25], ethylene glycol:choline chloride [16, 26], and urea:choline chloride [24] are some of the DESs used in these studies. Delignification efficiencies with DESs vary depending on the type of DES and conditions used, and can reach values that are comparable with conventional delignification

methods [15, 27]. On the other hand, it has been observed that delignification with DES using carboxylic acids with halide salts has a significantly faster delignification than the acid alone [28], showing that the halide anion is responsible for a catalytic effect [29]. Another study investigated the use of DES for wood chip fractionation and found that ethylene glycol:choline chloride could efficiently extract hemicelluloses and lignin to produce a cellulose-rich pulp, but this was not used for paper making [30]. More recent research developments include use of ternary DES mixtures, although they usually also not aim for making paper [31–34].

Only in a few studies investigating the use of deep eutectic solvents (DES) for pulping have fiber properties been examined. For example, it was shown that delignification using choline chloride-based DES can effectively delignify wood at lower temperatures and shorter cooking times than traditional kraft pulping [13], and the Eucalyptus fiber length was not reducing much [13]. However, the fibers were already very short at the start (0.81 mm), which might be due to the type of starting materials, being slabs of only about 20 mm. We hypothesize that in that work [13], the fibers were already damaged, so this paper does not provide relevant information for paper making. Similarly, although the work of Jablonski and co-workers showed importantly that fiber properties depend on the type of DES, they started with kraft lignin, [35], and no information on the delignification of wood was gained.

DES has been used for pulping of wood chips/slabs [13, 15, 36] and also for the delignification of Asplund fibers [37]. The length-weighted average fiber length of the resulting DES-fibers from Eucalyptus slabs was 0.68 mm achieving a pulping yield of 5.33% [13] while the degree of polymerization, (which is directly related with the fiber length) of the obtained fibers in other study (that uses Eucalyptus) was higher than that one from kraft pulp [15]. On the other hand, it has been shown that it is possible to obtain fibers with lengths of about 0.6 to 0.8 mm, a lignin content of about 14%, and a pulp yield of about 50% using DES for delignification of Asplund [37].

Typical kraft pulp fibers obtained from the pulping of spruce are much longer than other wood species while DES pulping provides smooth delignification. However, it is well known that there are several parameters that influence the paper quality. Hence, it can be expected that cooking of spruce wood chips with DES is a promising delignification method, but it is still unclear whether high enough quality cellulose fibers can be produced for making paper. Further research is needed to study the effect of operating conditions (cooking time, cooking temperature, type of lactic acid-based DES, type of agitation, water content, and addition of a preliminary impregnation step) on the DES pulping yield, the pulp lignin content, fiber length, and some other fiber properties. These aspects have been studied in this work.

## 2 Materials and methods

### 2.1 Materials

Lactic acid (90% aqueous solution) was purchased from VWR Chemicals, and pure lactic acid crystals were kindly donated by Corbion. Choline chloride (> 98%, solid phase), anhydrous sodium chloride (ACS reagent ≥ 99%, solid phase), sodium bromide (BioUltra ≥ 99.5%, solid phase), and sulfuric acid (95–98 ACS reagent) were purchased from Sigma Aldrich. Ethanol (100%) was purchased by Boom B.V. Wood chips (spruce) were supplied by Sappi Austria Produktions-GmbH & Co. KG. Moisture content in wood chips was quantified by weighing its mass on a wet basis and a dry basis (after oven drying) in triplicate. Mondi AG, Austria, supplied flash dried kraft pulp made of Norway spruce and Scotts pine in approximate ratio of 3:1. This sample, serving as reference, had a kappa number of approximately 45 (acid-insoluble lignin content of 9%).

### 2.2 Preparation of DES

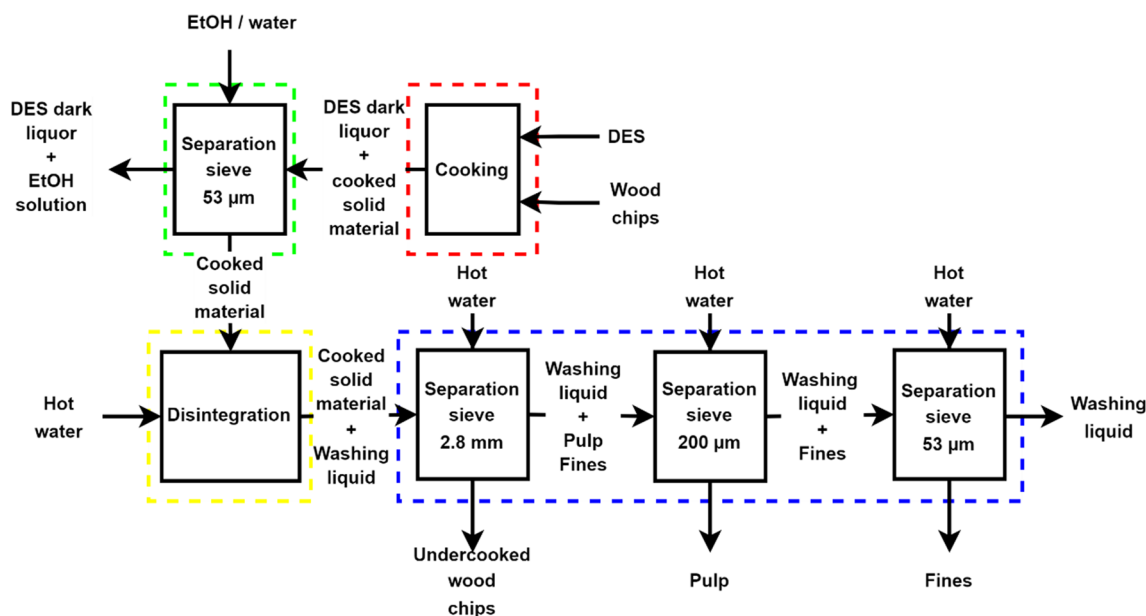
Lactic acid (LA) was used as the hydrogen bond donor (HBD) compound of the DES, whereas choline chloride (ChCl) was used as the main hydrogen bond acceptor (HBA). Sodium bromide (NaBr) and sodium chloride (NaCl) also were investigated as alternative salts to the HBA compound. The HBD compound was added to a 1-L glass

flask (typically 450 g of aqueous LA). Afterward, the HBA was added in a specific HBD:HBA mass ratio (10:1 unless mentioned otherwise, referred to as the weight of the aqueous LA) to the same flask. Then, the DES (HBD + HBA) was stirred with a magnetic stirring plate (Salmenkipp, at 360 rpm) for 1 h at room temperature. After stirring, LA:ChCl DES produces a single liquid phase, while in the LA:NaCl and LA:NaBr DESs, a fraction of the salt replacing the HBA remains solid.

### 2.3 DES-pulping of wood (spruce) chips

The DES-pulping of spruce chips consists of a cooking stage followed by separation of DES-dark liquor from cooked solid material (including a pre-washing of cooked solids with an ethanol solution), then is followed by a disintegration step (to liberate the delignified fibers) and then a screening stage to wash out the remaining DES-dark liquor entrapped in the solid cooked material and separate the undercooked wood chips, pulp, and fines using size-specific sieves (Fig. 1).

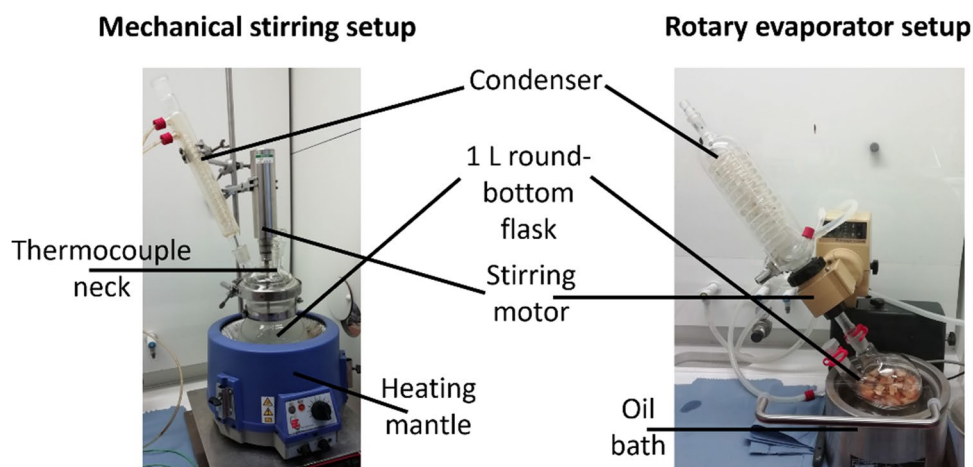
For cooking, 450 g of DES is added to the 1-L round-bottomed flask placed in the cooking setup (see Fig. 2, description in Sect. 2.3.1). Afterwards, the heating mantle, water flow (in the condenser), and stirring are turned on. Temperature is set to the cooking temperature (typically 130 °C), and the stirring is set at 360 rpm. Once the cooking temperature is reached, 45 g (dry basis) of wood chips are added into the round-bottom flask to achieve a



**Fig. 1** Stages of the DES-pulping process at lab-scale. The red dashed lines indicate the cooking step. The green dashed lines indicate the first wash and separation step. The yellow dashed lines indi-

cate the disintegration step, and the blue dashed lines indicate the washing and screening step

**Fig. 2** Cooking setups used in this work. Left side mechanical stirring setup, right side rotary evaporator setup



liquor-to-wood (L/W) mass ratio of 10:1, and the timer is started to measure the cooking time of the experiment (which usually was 3 h).

After cooking, the solid material and the DES dark-liquor were separated from each other by a 53- $\mu\text{m}$  sieve, while 1 L of a 50 wt% aqueous ethanol solution was used to wash the remaining DES dark-liquor from the solid cooked material (green dashed line stage in Fig. 1).

The cooked solid material from the sieve and 4 L of hot water (50–60 °C) were collected in a bucket while stirring with a crossed blade radial impeller and a IKA power control for 5 min at  $275 \pm 15$  rpm (yellow dashed line stage in Fig. 1). Next, the screening step was carried out using three different sieves (2.8 mm, 200, and 53  $\mu\text{m}$ ) to separate the undercooked wood chips, pulp (cellulose fibers), and fines (smaller cooked solid material of 200  $\mu\text{m}$ ) as is shown in Fig. 1. In the first stage of screening, a 2.8-mm sieve was used to separate the undercooked wood chips from the smaller cooked wood material (pulp and fines). The washing liquid containing the solids from the first screening stage were poured through a 200- $\mu\text{m}$  sieve to separate the pulp from the liquid and the smaller cooked wood material using about 8–10 L of hot water (50–60 °C). The pH of the collected washing liquid was measured with pH indicator paper. When the pH of the washing liquid was stable (indicating 6–7 pH), the pulp washing was stopped. The collected washing liquid was then poured through the 53- $\mu\text{m}$  sieve and washed with a maximum of 2 L of hot water (no more water is required to achieve a pH of the washing liquid of approximately 6–7), resulting in no more than 12 L of hot water being used in total for the screening step.

Undercooked wood chips (cooked solid wood material above 2.8 mm), pulp (cooked solid wood material between 2.8 mm and 200  $\mu\text{m}$ ), and fines (cooked solid wood material between 200 and 53  $\mu\text{m}$ ) were collected in separate glass bottles and oven-dried at 105 °C for at least 48 h for dry basis yields quantification.

### 2.3.1 Variations in cooking setups and conditions

Two different setups were used to investigate the effect of the operating conditions on the delignification of the wood chips. The first setup is a 1-L round-bottom flask with a 4-neck lid equipped with a heating mantle (Electrothermal), and mechanical stirring. An open condenser was applied for reflux of the produced vapor and a thermocouple. The motor was coupled to an impeller (half-moon style) within the round-bottom flask, and the thermocouple is set to a PID for temperature control with the heating mantle. The second setup comprised a rotary evaporator (Heidolph VV2000) equipped with an oil bath, 1-L round-bottom flask, and a condenser. The main difference was thus that in the first setup, mechanical stirring with an impeller was applied, and in the second setup, no internal stirring was done, but the whole vessel was rotated to induce mixing of the liquid. The temperature for delignification was controlled by the oil bath, while the 360-rpm rotation of the flask induced the mixing of the DES and the wood chips, and a condenser without receiving flask was applied to reflux the produced vapor during cooking.

All cooking experiments were performed at atmospheric pressure, and the effect of the cooking temperature on delignification and fiber length was investigated at 90, 110, 125, and 130 °C (fixing the liquor-to-wood ratio at 10:1 and 3 h of cooking). In another series of experiments, the cooking time was investigated at 2, 2.5, 3, 3.5, 4, and 4.5 h (fixing the liquor-to-wood ratio at 10:1 and the cooking temperature at 125 °C). Four levels of the liquor-to-wood ratio (5:1, 10:1, 15:1, and 20:1) were investigated at 130 °C during 4.5 h of cooking. The impact of the initial water content on the DES was studied at 2.4, 7.05, and 10.48 wt%. The water content on the DES was measured by Karl-fisher method once it was prepared. Experimentally, for an initial water content on the DES higher than 13 wt%, it was not possible to reach a temperature higher than 130 °C in the batch

cooking at atmospheric pressure while using the reflux condenser because of the vapor–liquid equilibrium limitations. In the mentioned experiments, LA:ChCl was applied in a 10:1 mass ratio.

The impact of changing the DES composition was investigated using sodium chloride and sodium bromide (within a DES with LA) in mass ratios of LA:NaCl of 100:1, 10:1, and 5:1 and LA:NaBr of 10:1 at 130 °C, 4 h of cooking, and a L/W ratio of 10:1. For all experiments mentioned so far, the setup with mechanical stirring was used.

The influence of the mechanical stirrer or the absence of that was studied for a range of conditions using the rotary evaporator setup (RE), using a varying L/W ratio at 130 °C, during 4 h of cooking. Additionally, the impact of an impregnation step (previous to the DES-cooking) was investigated. The wood chips were left in the DES at room temperature overnight before cooking. Then, the DES-cooking was performed at two different cooking times (2 and 3 h) in the RE setup at a L/W ratio of 10:1, and 130 °C.

## 2.4 Lignin content quantification

The lignin content (LC) on the spruce chips (after milling) and on all achieved pulps were experimentally quantified using the Klason method. Extractives and ashes were not quantified. Therefore, the reported LC in this work is the sum of acid-insoluble lignin (AIL), extractives, and ashes, unlike some other reports, where pulp is extensive washed with solvents before AIL quantification [38]. The LC quantification method was described elsewhere [37]. In this method,  $300 \pm 10$  mg material was impregnated with 3 mL of sulfuric acid (72 wt%) in a pressure tube at 30 °C, stirring the mixture every 10 min for 1 h. Then, 84 mL of milli-Q water was added to the pressure tube. The pressure tube was closed and placed in an autoclave for 1 h at 121 °C for hydrolysis. After hydrolysis, the tube was cooled down in a water bath till it reached room temperature. Afterwards, the hydrolyzed material was poured into a filter paper in a Buchner funnel setup. The material over the filter was rinsed with  $100 \pm 10$  mL of milli-Q water. Then, the filter with the solid materials was placed in an aluminum tray and dried in an oven at 105 °C. After drying, the solid material was weighed, and the lignin content was calculated as the percentage of dried solids related to the initial weight of the pulp sample.

## 2.5 Pulp fiber analysis

The fiber length of the achieved pulps and a benchmark pulp (unbleached Kraft pulp) was measured by Sappi (Austria) using an L&W Fiber tester Plus, at the French Pulp and Paper Research & Technical Center (CTP, France) in a MorFi analyzer, and at Mondi GmbH (Austria) with a

Valmet Fiber Image Analyzer (Valmet FS5). All samples were analyzed in Duplo. The length-weighted average of the fiber on the pulp, the coarseness, fiber shape, fibril area/perimeter, and crill index are reported in this work.

## 2.6 Definitions

The performance of the delignification process was quantified in all experiments by measuring the percentage of undercooked wood chips (UC), the pulp yield, and the percentage of fines of the screened solid material after the DES-cooking as follows:

$$\text{UWC (wt\%)} = \frac{\text{Mass of UWC (dry basis)}}{\text{Initial wood chips mass (dry basis)}} \times 100\%$$

$$\text{Pulp yield (wt\%)} = \frac{\text{Mass of pulp (dry basis)}}{\text{Initial wood chips mass (dry basis)}} \times 100\%$$

$$\text{Fines (wt\%)} = \frac{\text{Mass of fines (dry basis)}}{\text{Initial wood chips mass (dry basis)}} \times 100\%$$

On the other hand, the solids yield (ratio of solids after cooking compared to the amount of wood chips before cooking, all on dry basis) and wood conversion (amount of wood chips that is converted in pulp, fines, or dissolved compounds in DES) were also used to compare results (defined below).

$$\text{Solids yield (wt\%)} = \text{UWC} + \text{Pulp yield} + \text{Fines}$$

$$\text{Wood conversion (wt\%)} = \left( 1 - \frac{\text{Mass of UWC (dry basis)}}{\text{Initial wood chips mass (dry basis)}} \right) \times 100\%$$

The degree of delignification (DD) as well as the normalized fiber length (NFL) were calculated similar as they were defined elsewhere [37]:

$$\text{DD(-)} = \frac{\text{LC}_{\text{wood}} - \text{LC}_{\text{pulp}}}{\text{LC}_{\text{wood}}}$$

$$\text{NFL(-)} = \frac{\text{FL}_{\text{pulp}}}{\text{FL}_{\text{ref}}}$$

For calculation of the DD, the lignin content ( $\text{LC}_{\text{wood}}$ ) in the milled wood (from spruce chips) and the lignin content on the achieved pulp ( $\text{LC}_{\text{pulp}}$ ) was used.

For comparison purposes, the fiber length was normalized to the length of the reference fiber from the Kraft pulp (2.349 mm). The lowest normalized fiber length was achieved at the lowest value for which fibers were still considered as pulp fibers, which is 0.2 mm. At this length,  $\text{NFL}_{\text{min}} = 0.2/2.349 = 0.08$ . Particles with sizes smaller than 0.2 mm are defined as fines. The maximum value of the NFL

that could be obtained was  $2.8/2.349 = 1.19$ , corresponding to the size of the sieve used during the screening of the cooked material.

As a quick measure of the quality of fibers in terms of the DD and NFL, the quality parameter  $Q$  was introduced recently [37] as follows:

$$Q = DD \times NFL$$

Naturally, during the delignification process, the value of DD will increase, while NFL will decrease. Ideally, DD can increase without too much fiber length loss. However, for comparison purposes, the DD, NFL, and finally the  $Q$  value of kraft pulp are calculated as benchmarks.

Next to the DD and the NFL, several other fiber quality parameters have been measured during the fiber analyses (L&W Fiber tester Plus). These include coarseness (how much mass per length of fiber), shape factor (how much the fiber it is bent), crill index (the amount of fiber fragments that can interact with other fibers), fibril area, and fibril perimeter (fibrils are small particles, distinguish between fibrils and fibers).

## 3 Results and discussion

### 3.1 Impact of DES-cooking operating conditions on the spruce chips delignification

The impact of cooking temperature, cooking time, liquor-to-wood (L/W) ratio, and initial water content on the performance of the DES-cooking of spruce chips was investigated using lactic acid:choline chloride DES at a mass ratio of 10:1 in the mechanical stirring (MS) setup. The results are displayed in Fig. 3, and include the percentage of undercooked wood chips (UWC), the pulp yield, the percentage of fines, the lignin content (LC), and the fiber length on the pulp. For comparison, the lignin content on the raw material (spruce chips) was measured experimentally, giving a  $29.05 \pm 0.05$  wt%. Two batches of spruce chips were used, the first one with a water content of  $31.5 \pm 0.2$  wt% and the second batch with  $35.2 \pm 0.4$  wt%.

In Figure 3(i), it is observed that with an increase in the cooking temperature (from 90 to 130 °C), both the undercooked wood chips percentage and the lignin content on the pulp decrease, while the pulp yield increases. While these trends are well in line with expectations due to higher reaction rates at higher temperatures, examining the fiber length as function of reaction temperature shows that the fiber length is increasing with increasing reaction temperature, and this is a bit more complex to explain. At higher temperatures, the breakdown reactions of the cellulose are expected to be more predominant. However, the fiber length increase

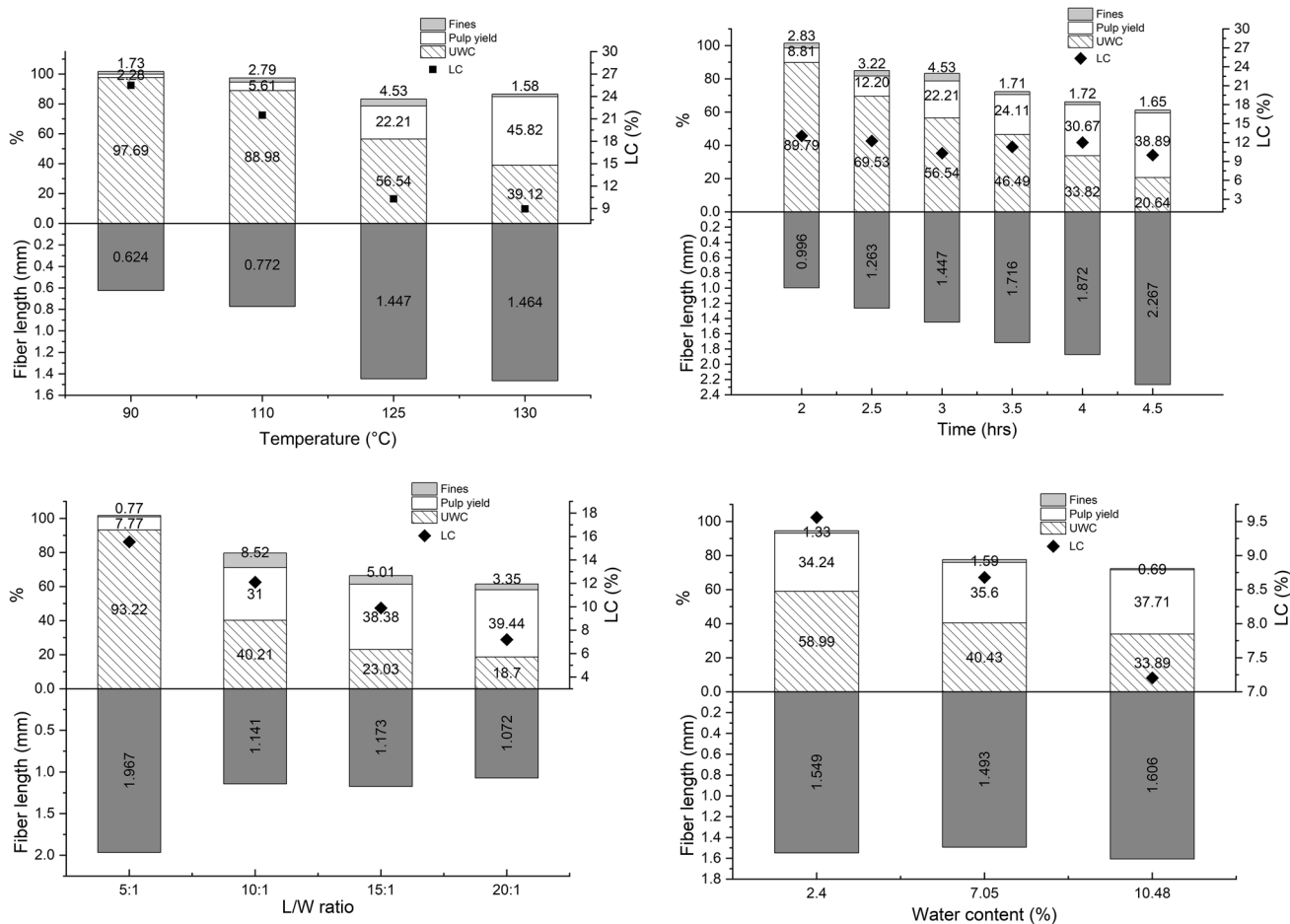
is most likely correlated with the larger fraction of the wood that ends up as pulp fraction. At low reaction temperature, hardly any pulp is formed, and only smaller fibers close to the surface of the wood chips are liberated. These surface fibers are expected to be shorter since the wood, thus the fibers, are cut to form chips. At the higher temperatures, the delignification is much more significant, resulting in larger fibers also being liberated from deeper in the matrix of the chip. Some aspects of the pulping process that have important influences on the delignification include the following steps: the penetration of the DES into the internal structure of wood through the lumen. Then, once the DES is in contact with the internal cell walls, the cleavage of ether bonds in cellulose, and between lignin and cellulose, as well as in lignin (such as the characteristic  $\beta$ -O-4 ether bonds) takes place if enough energy is provided. Afterwards, the liberated lignin polymers are solubilized into the DES and transported from the DES in the lumen to the DES in the bulk of the liquid phase [39, 40].

The sequence of these steps is affected by temperature, as high temperature decreases the viscosity of the DES and consequently promotes its penetration into the internal wood structure. Also, the high temperature provides more energy for the cleavage of the ether [29, 41]. In addition, the solubility of solutes into liquids increases with the increase of the temperature. In this case, the derived lignin polymers solubilize better into the DES at a high temperature.

Since more bonds are cleaved and the mass transport is improved at high temperature (130 °C), as compared to the low temperature (90 °C), more fibers are liberated from the wood matrix. Thus giving a higher pulp yield. Besides, the lignin content of the fibers and thus pulp decreases because of the increased reaction rate at higher temperatures. The quality parameter  $Q$  that relates the degree of delignification and the normalized fiber length is displayed in Fig. 4.

Next to the reaction rates and mass transfer, one additional aspect might influence the fiber length, which is the beating of the wood by the impeller. In the DES-cooking at 90 and 110 °C, a very high lignin content (25.5 and 21.5 wt%) is combined with a low pulp yield (2.20 and 5.61 wt%, respectively), which hardly would not lead to liberation of fibers, and the short fiber length (0.624 and 0.772 mm) achieved might be due to another fiber liberation mechanism, i.e., some of the fibers were liberated due to the beating of the impeller with the spruce chips during stirring. To evaluate this hypothesis, also experiments were done using the rotatory-evaporator setup, these results are shown in Fig. 5.

Figure 3(ii) shows the effect of the cooking time on the DES-cooking of spruce chips in a L/W ratio of 10:1 and a cooking temperature of 125 °C. At short cooking times, it was observed that delignification of the wood allows only the liberation of small fibers (0.996 and 1.263 mm at 2 and 2.5 h of cooking) and thus yielding only small amounts of pulp



**Fig. 3** The percentage of fines, pulp yield, undercooked wood chips, pulp fiber length, and LC studied as function of the temperature (i) at L/W ratio of 10:1 during 3 h of cooking; the cooking time (ii) at

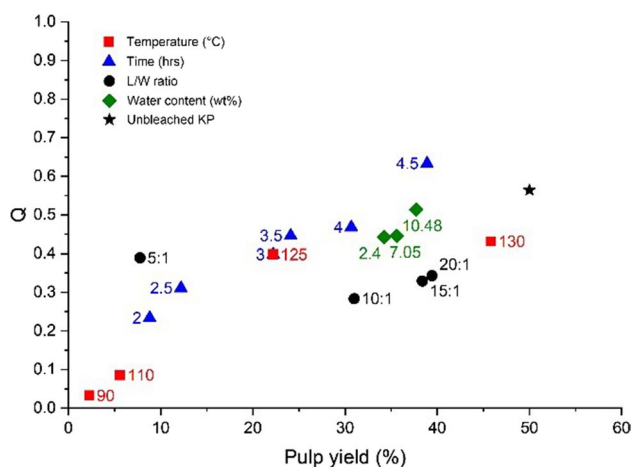
L/W ratio of 10:1 and 125 °C; the L/W (iii) at 130 °C during 4.5 h; and the initial water content in the DES (iv) at L/W of 10:1, 130 °C during 3 h

(8.81 and 12.20 wt% at 2 and 2.5 h of cooking) with the wood chips remaining almost intact (89.79 wt% of the wood chips is undercooked at 2 h of cooking). Apparently, the contact time of the DES with the wood chips is too short to cleave a significant amount of the ether bonds in the lignin. In addition, since the lumen of the internal wood structure fills gradually, and no pressure is applied, the time of contact of the DES and the internal wood walls is not uniform over the whole chip.

Over the cooking time, several continuous and successively processes occur. Fibers are liberated from the wood due to the cleavage of the  $\beta$ -O-4 bonds. Liberation of the fibers from the wood matrix makes them more accessible to the DES, which leads to their delignification and degradation. A previous work [37] that investigated DES-cooking of Asplund fibers (instead wood chips) showed how fast the shortening of Asplund occurs (reduction of 53.67% of its length after 30 min of cooking) at the same conditions of this work. Due to the shortening of the cellulose fiber, the fibers become in fines (particles with a size smaller than 200  $\mu$ m

and higher than 53  $\mu$ m). Then, the fines remain degrading until producing oligomers and subproducts. Also, the derived lignin polymers that come from the cleavage of their ether bonds are solubilized into the DES and may continue depolymerizing and repolymerizing.

Thus, with increasing cooking time the pulp yield increases, the UWC percentage decreases, and the solids yield (UWC + pulp + fines) decreases as is shown in Fig. 3(ii). At 2.5 h of cooking, the solids yield is 84.95 wt%, while at 4 h of cooking is 66.21 wt%. The solids yield in the experiment at a cooking time of 2 h was 101.43 wt%. This result suggests there is DES entrapped in the UWC after the washing step. Elisabet Brännvall et al. showed [42] that a portion of the DES-dark liquor (with significant lignin content) remains entrapped within the wood chips after cooking in kraft pulping. Hence, the UWC of this set of experiments was rinsed again. They were put in a bucket with hot water (4 L) overnight, and then they were poured over a sieve of 53  $\mu$ m, and 3 L more of hot water was used to rinse it. Then,



**Fig. 4** Quantification of the quality of the achieved fibers through the parameter  $Q$  for the DES-pulps achieved at the operational conditions investigated. Cooking temperature (red squares) at L/W ratio of 10:1 during 3 h of cooking. Cooking time (blue triangles) at L/W ratio of 10:1 and 125 °C. L/W ratio (black circles) at 130 °C during 4.5 h. Water content on the prepared DES (green diamonds) at L/W of 10:1, 130 °C during 3 h. The  $Q$  value for unbleached kraft pulp (black star) was calculated to compare with the achieved pulps

the washed UWC were oven-dried for 48 h, where its weight remained constant. After the re-washing and drying steps, the UWC percentage was reduced from 89.79 wt% (no re-washed) to 82.14 wt%. This result proves that there is DES dark-liquor entrapped in the UWC, which overestimates the reported values of the percentage of UWC (and subsequently the wood conversion and solid yield) in this work.

Prolonged cooking time, such as 3.5 or 4.5 h, allows the liberation of long fibers (1.716 and 2.267 mm, respectively). At these cooking time, the DES penetrates to a greater extend into the internal wood structure promoting contact with the wood walls for reactive cleavage of lignin ether bonds.

The lignin content on the achieved pulps remains near 12 wt% for every cooking time evaluated. Meaning an actual amount of about 8.6 wt% due to not extracting extractives prior; in separate Soxhlet experiment, 3.44 wt% extractives were removed. However, it was observed that pulp yield increased with cooking time. There is not a single to explain why the LC does not drop below 12 wt%, but the interplay between delignification, fiber release, and degradation may help to explain this effect. The more fiber released, the higher the lignin content in the DES-dark liquor. The DES then interacts with the solubilized polymers of lignin (depolymerizing and polymerizing them), and this reduces the availability of DES to interact with the cellulose of the fiber to degrade it (and thus avoiding significant fiber shortening).

The increment of the L/W ratio impacts the delignification of the wood chips positively, as is shown in Fig. 3(iii).

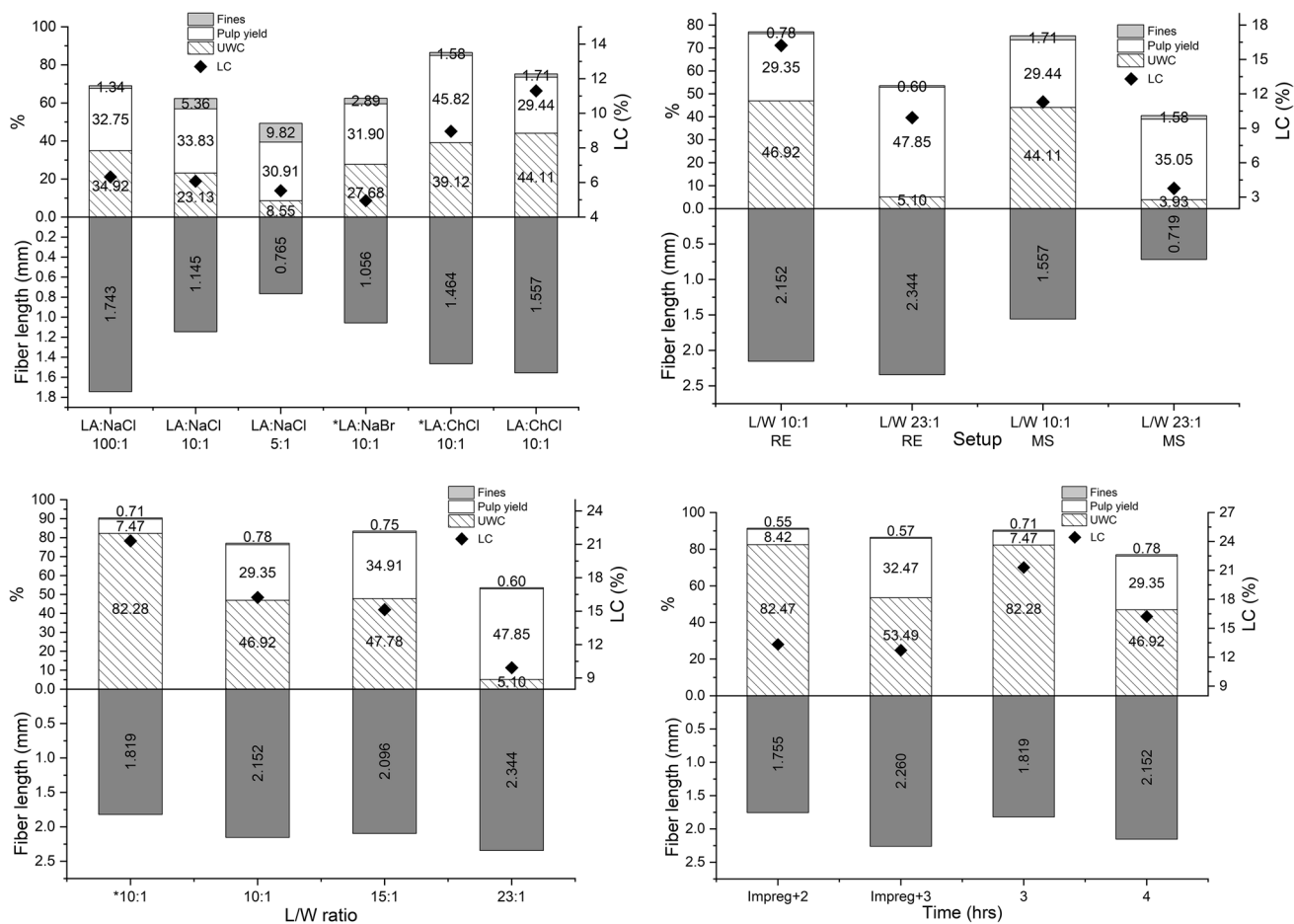
As the L/W ratio increases from 5:1 to 20:1, the pulp yield increases from 7.77 to 39.44 wt%, while the percentage of UWC decreases from 93.22 to 18.7 wt%. The L/W ratio mainly affects the mass transfer process. A high L/W ratio provides a higher volume of DES as compared to the wood chips. Therefore, the lignin molecules dissolved into the DES after cleavage of the  $\beta$ -O-4 ether bonds will be more diluted at a high L/W ratio than at low L/W ratio, providing a higher driving force for lignin transport from the internal wood structure towards the bulk of the DES in the reactor. Besides, also the lignin content on the pulp is reduced due to the higher driving force as the L/W ratio increases. The most significant impact of the L/W was achieved between the L/W ratio of 5:1 and 10:1. However, it should be considered that in industrial processing conditions in scaled-up processes, mass-transfer conditions are better due to static pressure, and most likely lower L/W ratios are sufficient, while operation under flow conditions and recycling of solvent may also be considered.

The fiber length was considerably affected by increasing the L/W ratio from 5:1 to 10:1. It was reduced from 1.967 to 1.141 mm. A high L/W ratio promotes dilution of the solubilized lignin in the DES-dark liquor, making the DES more available to interact with both, the solubilized lignin and the cellulose fiber, resulting in smaller fibers. Furthermore, it should be considered that the mechanical impact of the beating of the impeller with the wood chips and fibers is another cause of the shortening. This source of shortening is evaluated and discussed in Fig. 5(ii).

The initial water content on DES does not affect the fiber length achieved after cooking (Fig. 3(iv)). The fiber length remains around 1.5 mm (in a DES-cooking at 130 °C with a L/W ratio of 10:1 during 3 h) in the range of initial water content on the DES investigated, 2.4 to 10.48 wt%. For an increasing initial water content from 2.4 to 10.48 wt%, it was observed that the pulp yield increases with 3.46 wt%, while the percentage of UWC decreases with 25.1 wt%. Although the conversion of wood increases from 41.01 to 66.11 wt%, the pulp yield increased by 3.46%. It indicates 21.64 wt% of the pulp has dissolved into the DES (as derived polymers from degradation of lignin, hemicellulose, and cellulose). Furthermore, the fact that the wood conversion increases in a higher proportion than pulp yield suggests that the presence of water into the DES significantly promotes the cleavage of  $\beta$ -O-4 bonds of lignin. Further increasing the initial water content is of limited interest, because adding water will increase the vapor pressure significantly at operational temperatures, and one of the benefits of using DES instead of aqueous media, such as sulfite or sulfide as in current industrial processes, is the low vapor pressure.

The presence of water in the DES provides lower viscosity of the DES as compared with the DES without any





**Fig. 5** The effect of the salts within the DES with LA (i) in the setup with mechanical stirring, the type of mixing (ii) provided by mechanical stirring (MS) or Rotary flask in a Rotary-evaporator (RE), the L/W ratio (iii), and the addition of a previous impregnation stage (iv)

to cooking, on the percentage of fines, pulp yield, undercook wood chips, and fiber length (on pulp). The following conditions were fixed, at least in the plot it is indicated the contrary: 4 h of cooking, a L/W ratio of 10:1, 130 °C in the RE setup. \*Indicates 3 h of cooking

water content. Therefore, the penetration rate of DES and water mixture into the wood chip is promoted. Water is involved in several reactions during the cooking process. Esterification of the OH group of the ChCl with the lactic acid may occur [43]. However, because the water is already present in the DES, the forward reaction of the esterification (hydrolysis) is less favored as esterifications are equilibrium reactions where water is produced. Hydrolysis of dimers or trimers of the LA may also occur because of the initial water content on the DES during cooking [44]. Both hydrolysis reactions avoid the consumption of the ChCl and LA molecules on side reactions, leading to these molecules of DES be available for delignification during cooking. Hence, both pulp yield and LC are promoted at a higher water content on the DES.

In Fig. 4, the *Q* parameter vs the pulp yield is shown to understand the impact among the different

operating conditions evaluated on the properties of the pulp achieved. The *Q* parameter of the unbleached Kraft pulp (KP) was included in Fig. 4 as a benchmark (*Q* = 0.56 and pulp yield = 50 wt%).

Since a cooking temperature (red squares in Fig. 4) lower than 110 °C does not provide enough energy for delignification and fiber liberation, low values of the *Q* parameter and pulp yield are achieved (lower than 0.1 and 10 wt%, respectively). On the other hand, although the *Q* parameter remains around 0.4 for a cooking temperature between 125 and 130 °C, the pulp yield significantly increases from 22.21 to 45.82 wt% in the same range of temperatures. The increase in the cooking temperature of 5 °C allowed increasing the pulp yield 23.61 wt% without a detrimental effect on the quality parameter of the cellulose fiber.

The cooking time (blue triangles in Fig. 4) also provides significant changes in both *Q* and pulp yield. It was possible

to achieve a value of  $Q$  of 0.63 (at 4.5 h of cooking) which is higher than the value achieved for the unbleached KP. Nevertheless, the pulp yield is 38.89 wt% at the highest cooking time, while for the unbleached KP is around 50 wt%. At 4.5 h of cooking, the fiber length and the LC (2.267 mm, and 7.66 wt%) are slightly lower than those in the unbleached KP (2.349 mm and 9 wt%).

Unlike the cooking temperature and time, the L/W ratio (black circles in Fig. 4) has a negligible impact on the  $Q$  parameter. The  $Q$  parameter remains around 0.35 for the L/W ratio from 5:1 to 20:1, while the pulp yield increases from 7.77 wt% (at a L/W ratio of 5:1) to 39.44 wt% (at a L/W ratio of 20:1). On the other hand, the initial water content on the DES slightly affects both the  $Q$  parameter and the pulp yield.

The operating conditions that provide similar values of the pulp yield and  $Q$  parameter as the unbleached KP were at 130 °C (at a L/W ratio of 10:1 and 3 h of cooking) and at 4.5 h of cooking time (at a L/W ratio of 10:1 and 125 °C).

### 3.2 Further improvements on DES-cooking for spruce chips delignification

After knowing the effect of the operating conditions of DES-cooking on the spruce chips delignification, several trials were made looking to improve the quality of the pulp and get additional insights into the DES-cooking of spruce chips. For that set of experiments, the cooking temperature was set at 130 °C, the L/W ratio at 10:1, and the cooking time at 4 h.

Two alternatives for choline chloride, sodium chloride (NaCl) and sodium bromide (NaBr), were used to produce DES mixtures with LA. The impact of each mixture on the DES-cooking of spruce chips is evaluated and compared with the LA:ChCl DES (Fig. 5 (i)). The DES-cooking at three LA:NaCl ratios (100:1, 10:1, and 5:1) produced a similar amount of pulp (around 32 wt%). However, it was observed that the higher the amount of NaCl, the faster the delignification and cellulose degradation rate resulting in a lower amount of UWC. The wood conversion increased from 65.08 wt% at 100:1 LA:NaCl ratio to 91.45 wt% at 5:1 LA:NaCl ratio, whereas the fiber length decreased from 1.743 to 0.765 mm, respectively. The high wood conversion (which means low UWC percentage) is related to the rate of the cleavage lignin bonds, while both the shortening of the cellulose fibers and the increase of the amount of fines are related to the cellulose degradation rate. On the other hand, both the LC and the pulp yield remained constant at the three LA:NaCl ratios evaluated. The pulp yield remains around 32 wt%, while the LC is about 6 wt%. It suggests that, although the reaction rate (delignification and cellulose degradation) changes depending on the LA:NaCl ratio used, the interplay between the conversion of wood chips into pulp and the conversion of pulp into fines (and dissolved compounds

into the DES) is comparable in the DES-cooking among the LA:NaCl ratios.

Comparing the results achieved by using LA:NaCl with those achieved using LA:ChCl (both at 10:1 ratio and the same conditions), it was observed that reaction rates by using NaCl are faster than by using LA:ChCl. Using NaCl provides a higher wood conversion (76.87 wt%), pulp yield (33.83 wt%), fines (5.36 wt%), and a lower LC (6 wt%). This indicates faster rate of the cleavage of the  $\beta$ -O-4 bonds of lignin as compared to the results achieved with ChCl (55.89, 29.44, 1.71, and 8.95 wt%, respectively). The lower fiber length (1.145 mm) obtained after the DES-cooking with NaCl than the fiber length (1.557 mm) achieved with ChCl, suggests a faster cellulose degradation by using NaCl. Previous research showed that in a DES containing LA, the sodium provides higher wood conversion than the anion choline with chloride [28], which agrees with the results in this work.

The DES-cooking of spruce chips using LA:NaBr provides even faster reaction rates than using LA:NaCl or LA:ChCl. Despite the solids yield after cooking was similar by using NaBr or NaCl (62 wt%), the wood conversion (72.32 wt%) and the LC (4.95 wt%) were slightly lower when is used NaBr than using NaCl (76.87 wt% and 6.07 wt%, respectively). It indicates that the reaction rate of lignin cleavage is faster by using LA:NaBr than using LA:NaCl, due to the cooking time was 3 h in the DES-cooking with LA:NaBr as compare to 4 h of cooking with LA:NaCl. Similarly, the fiber length was 1.056 mm using LA:NaBr, while it was 1.145 mm using LA:NaCl (Fig. 5(i)). Considering the difference of 1 h in the cooking time implies that the cellulose degradation rate is faster using LA:NaBr than LA:NaCl.

The fact that the wood conversion (60.88 wt%) and LC (8.95 wt%) are lower using ChCl than using NaBr, while the fiber length (1.464 mm) is higher using ChCl than using NaBr (72.32%, 4.95%, and 1.056 mm, respectively), at the same operating conditions of DES-cooking (and LA:HBA ratio of 10:1), implies that both the lignin cleavage and the cellulose degradation rates are faster in the DES-cooking with NaBr than NaCl.

Although both DESs, LA:NaCl and LA:NaBr (at ratio of 10:1), provide faster delignification than LA:ChCl, these DESs have a detrimental impact on the fiber length because cellulose degradation is also faster using these DESs. However, when a low amount of NaCl is used in the LA:NaCl DES (such as 100:1 ratio), similar wood conversion and pulp yield among the DESs evaluated are achieved. In contrast, a slightly higher fiber length is provided by using LA:NaCl than using LA:ChCl.

As was mentioned before, it is suspected that the beating of the impeller during the stirring in the DES-cooking breaks down the wood chips and the produced fibers. Pérez et al. [37], showed this detrimental impact on the DES-cooking

of Asplund fibers, comparing the results using two setups, the mechanical stirring (MS) setup and the rotary-evaporator setup (RE). In this work, both setups were used to prove and quantify the impact of the MS on the DES-cooking of spruce chips, and the results are shown in Fig. 4(ii). The experiments were performed at two levels of the L/W ratio (10:1 and 23:1). At a 10:1 L/W ratio, the percentage of UWC, the pulp yield, and amount of fines (around 45 wt%, 29 wt%, and 1 wt%, respectively) were similar for both setups. However, the achieved fiber length using the RE setup was 2.152 mm, while in the MS setup was 1.557 mm, supporting the detrimental effect that the MS has on the fiber length during DES-cooking. Similar results were obtained at a L/W ratio of 23:1, where the fiber length was 2.344 mm in the RE setup, whereas it was 0.719 mm in the MS setup. The shortening of the cellulose fiber has a bigger impact at the L/W ratio of 23:1 than in the L/W of 10:1.

Additionally, at the L/W ratio of 23:1, the percentage of UWC (5.1 wt%), the pulp yield (47.85 wt%), and the LC (9.93 wt%) were higher in the RE setup, than in the MS setup (3.93 wt%, 35.05 wt%, and 3.77 wt%, respectively). It is because the impeller breaks down small pieces of the wood chips and weakens and breaks down the liberated cellulose fibers. Hence, in the MS setup, the shrinking of the spruce chips and the shortening of the cellulose fiber are both due to the delignification and cellulose degradation as well the fiber breaking by the impeller. This effect is magnified when the L/W ratio is 23:1 because, in this condition, there is more distance among the wood chips than at a 10:1 ratio. A higher free space between the chips allows the impeller to drag the chips more easily and, consequently, beat them. On the contrary, when the L/W ratio is 10:1, the free space among wood chips is reduced, and the wood chips move like one solid body, where only the wood chips near the impeller are beaten.

Another interesting result to notice from Fig. 5(ii) is the opposite trends in the fiber length between both setups when the L/W varies. In Fig. 3(iii) and Fig. 5(ii), the fiber length decreases as the L/W increases (from 10:1 to 23:1) in the MS setup, while in the RE setup (Fig. 5(ii)), it seems like the fiber length is slightly increasing as the L/W rises. Confirming this trend in the RE setup, the DES-cooking was performed at L/W ratios of 10:1, 15:1, and 23:1 at 130 °C during 4 h of cooking (Fig. 5(iii)). The trends in UWC, pulp yield, fines, and LC were similar using both setups. However, it was proven that the trend of the fiber length achieved in the MS setup is opposite to the one achieved in the RE setup. When the MS setup is used, the conversion of wood is favored by the breakdown of the wood chips, leading the broken pieces of the wood chips to increase the area of contact between the DES and the wood, and consequently speeding up the delignification rate. Nevertheless, in the DES-cooking using the RE setup, there was no breaking down of wood chips, allowing to observe the effect of the

DES-delignification only. In the RE setup, it was observed that the fiber length slightly increases as the L/W ratio rises. At the L/W ratio of 23:1, it was possible to achieve cellulose fibers with low LC (9.93 wt%), and a pulp yield (47.58 wt%), and fiber length (2.344 mm) comparable to the unbleached Kraft pulp (5 wt%, 50 wt%, and 2.349 mm, respectively).

An additional variable investigated in this work was the effect of the impregnation step previous to the DES-cooking in the RE setup. The wood chips were in contact with the DES (at L/W ratio of 10:1) overnight at room temperature to allow full penetration of the DES into the internal wood structure without reaction. The experiments were performed at 130 °C with LA:ChCl (10:1) DES at 2 and 3 h of cooking, comparing to the DES-cooking experimental results at the same conditions and setup without the impregnation step (Fig. 5(iv)). It was observed that in 2 h of cooking with impregnation, similar results are achieved (in terms of UWC, pulp yield, fines, and fiber length) as compared to 3 h of cooking without impregnation. However, the LC (13.3 wt%) obtained in the pulp from the DES-cooking with the previous impregnation of the spruce chips is lower than the LC (21.31 wt%) in the process without impregnation. For 3 h of cooking with impregnation, a slightly higher pulp yield (32.47 wt%), lower LC (12.73 wt%), and slightly higher fiber length (2.260 mm) are achieved as compared with 4 h of cooking without impregnation (29.35 wt%, 16.23 wt%, and 2.152 mm). The addition of an impregnation step to the DES-cooking of the wood chips is advantageous because it reduces the cooking time and allows a higher delignification without detrimental impact on the fiber length. It allows achieving fiber with higher length as compared to the process without impregnation.

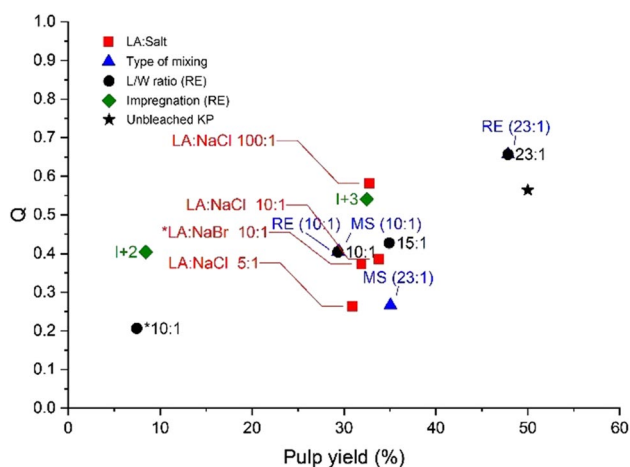
In the DES-cooking without the previous impregnation step, the DES penetration into the internal wood structure occurs simultaneously with the delignification of wood, and at atmospheric pressure, the impregnation might be slow. In the DES-cooking with impregnation step, the internal structure of wood appears better filled with cooking liquor before the delignification begins. When penetration of DES into the internal wood structure happens simultaneously with delignification, the contact time of the DES with the internal wood walls differs from the point of penetration towards the most internal point of the wood. The contact time will be higher at the initial penetration point compared to most internal wood point. It leads to the delignification occurring progressively in the wood lumen direction where the DES is penetrating. Therefore, the wood section near the penetration point has a higher delignification and subsequent higher degradation of the released fibers than the most internal section of the wood chip. On the other hand, when the lumen is filled to a larger extent with DES before cooking, the delignification occurs more homogeneously in the longitudinal direction of the lumen, providing more

homogeneous liberation of fibers from the whole internal wood structure simultaneously.

Since the penetration has a beneficial impact on the DES-cooking, it could be considered to include in the industrial sized process. Alternatively, to improve DES-penetration into the internal wood structure, using a pressurized reactor to allow faster penetration of the DES may be considered.

The effects of the salt in the DES with LA, the kind of mixing, the L/W ratio (using the RE setup), and the addition of the impregnation step on the DES-cooking of spruce chips were also quantified in terms of the quality ( $Q$ ) parameter as is shown in Fig. 6. It was observed that when the type of salt was varied at otherwise constant conditions, the  $Q$  parameter varies while the yield remained similar. Also changing the LA:salt ratio in a series with NaCl experiments influenced on the  $Q$  parameter but kept similar pulp yields. The pulp yields did vary significantly with variations in the operating conditions. The operating conditions of the DES-cooking on all trials for evaluating the effect of the salt remained fixed, and the pulp yield slightly varied (from 30 to 34 wt%), as is showed in the red squares of Fig. 6.

The type of mixing (MS or RE) showed a negligible impact on the  $Q$  parameter (around 0.4) and pulp yield (approximately 29 wt%) at a L/W ratio of 10:1 at the experimental conditions tested (blue triangles in Fig. 5). On the other hand, at a L/W ratio of 23:1, a detrimental impact on the  $Q$  parameter (0.27) and pulp yield (35.5 wt%) was observed in the MS setup, while its effect on both  $Q$  (0.66) and pulp yield (47.85 wt%) was significantly better at the same L/W ratio in the RE setup. Additionally, it is observed the higher the L/W ratio is (using the RE setup), the higher the pulp yield and  $Q$  parameter (black circles in Fig. 5) will be. Even at a 23:1 L/W ratio, a value of the  $Q$  parameter



**Fig. 6** Quality of the pulp (through the  $Q$  parameter) obtained for the different salts evaluated (red squares), the type of mixing (blue triangles), the L/W ratio (black circles), and the pulping with an impregnation step (green diamonds). The  $Q$  value for unbleached kraft pulp (black star) was calculated to compare with the achieved pulps

of 0.66 was achieved, slightly higher than the  $Q$  parameter (0.57) of the unbleached Kraft pulp at similar pulp yield (47.84 wt% and 50 wt%, respectively).

The value of the  $Q$  parameter at 3 h of cooking with impregnation (green diamonds) is 0.54, which is near the value of the benchmark, the unbleached Kraft pulp (0.56). However, the pulp yield is still lower, at 32 wt%, as compared to 50 wt% in the KP (Fig. 6). Nevertheless, it is possible to improve the  $Q$  parameter and the pulp yield by increasing the cooking time, as shown in Fig. 4 (blue triangles).

### 3.3 Effect of the DES-cooking on the fiber properties

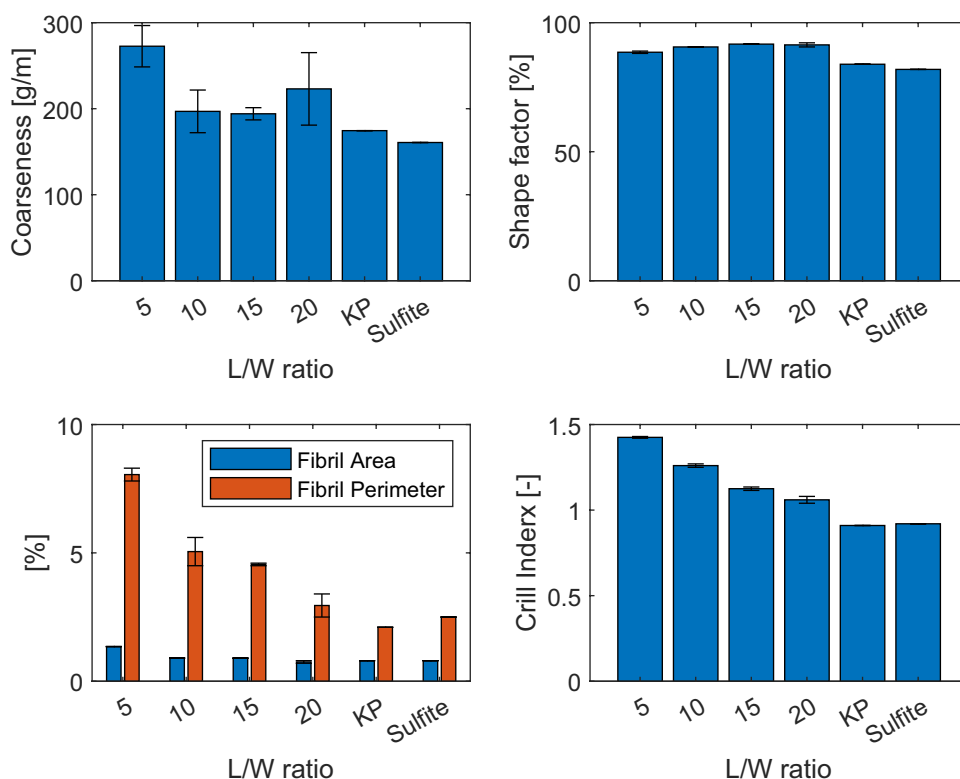
In addition, the effect of the evaluated operating conditions on the fiber properties of the obtained pulp, coarseness, shape, fibril area/perimeter, and crill index is shown in Fig. 7 and compared to unbleached softwood KP and spruce/beech sulfite pulp.

The coarseness of the fibers obtained at the investigated liquor to wood ratios (5, 10, 15, and 20) has an average value of  $221.68 \pm 31.52$  g/m, which is slightly higher than the value of KP and sulfite pulp (Fig. 7i). Since the coarseness is the mass per fiber length, it can be assumed that the higher value of coarseness in the DES pulp fibers is due to the higher LC of these fibers (Fig. 3(iii)) compared to KP and sulfite pulp.

The shape factor is a measure of how much the fiber is bent (i.e., a shape factor of 90% indicates the fiber is fairly straight). Fibers from KP and sulfite pulp are more curled than the resulting fibers from DES pulp (Fig. 7(ii), Figure S1(ii) and Figure S2(ii)). However, the shape factor of the fibers obtained at a cooking temperature of 90 °C is comparable to the shape factor of both KP and sulfite pulp fibers. Furthermore, the cooking time did not affect the shape factor of the resulting fibers (Figure S2(ii)). For this parameter, important information is that at larger scale productions, typically lower shape factors are obtained than with laboratory experimentation due to processing of the fibers, such as pumping in industrial operation that may damage the fibers.

The fibril area/perimeter of the resulting DES pulp fibers decreased with increasing temperature and liquor/wood ratio (Figure S1(iii) and Fig. 7(iii)). In addition, the fibril perimeter of the DES pulp fiber was always higher than that of the KP and sulfite pulp fibers, while the fibril area of the DES pulp fiber was comparable to that of the KP and sulfite pulp fibers in all ranges of temperatures and liquor/wood ratios studied (except for the lowest temperature and liquor/wood ratio). On the other hand, the fibril perimeter was not affected at cooking times of 2 to 4 h, where it remained close to a value of 4%. However, it decreased dramatically to a value of 2.9 at a cooking time of 4.5 h. Despite this decrease in fibril perimeter in the DES pulp fiber, the values of this fiber property always remained higher than those of the KP and sulfite pulp fibers (Figure S2(iii)).

**Fig. 7** Impact of the liquor to wood ratio on the coarseness, shape factor, fibril area/perimeter, and crill index of the obtained pulp fibers after DES-pulping. DES-cooking was performed at 130 °C during 4.5 h



The crill index tells us how many fragments are present in the pulp that can interact with other fibers to make the surface more binding. A higher crill factor would result in better bonding in the sheet, which would have a positive effect on the paper properties. The crill index of DES pulp fibers was always slightly higher than that of KP and sulfite pulp (Fig. 7(iv), Figure S1(iv), and Figure S2(iv)). However, it was found that the crill index of DES pulp decreased with increasing cooking temperature and liquor to wood ratio. On the other hand, the crill index of the DES pulp fibers was not affected by the increase in cooking time (from 2 to 4.5 h).

Based on these results, indicating that fiber properties comparable to sulfite pulp can be achieved, and for some parameters even KP, it is suggested that DES-based pulping is further researched on larger scale in pilot facilities, so that larger portions of fibers can be applied in paper sheet making and next to the fiber parameters, also qualitative and quantitative analysis of the final paper quality can be performed.

## 4 Conclusions

Delignification of spruce chips by using lactic acid:choline chloride deep eutectic solvent is a promising technology to achieve pulp with fibers of a quality that approaches the current standards in the paper

industry, with some of the parameters such as the crill factor even slightly higher. The cooking time and the cooking temperature were the operating conditions that provide the most significant changes on the pulp yield and quality of the achieved cellulose fibers. On the other hand, addition of an impregnation step before the cooking resulted beneficial in terms of the pulp yield and quality of the fibers.

Fibers from DES pulp showed a slightly higher crill index, shape factor, and fibril perimeter than the reference kraft and sulfite pulps, indicating that DES pulp has the potential to produce higher quality paper than kraft and sulfite. However, in the case of shape factor, it is known that laboratory produced pulps will always have a higher shape factor (straighter fibers) than industrially produced pulps, as the pulp is pumped through several stages on an industrial scale (the more you pump the fibers, the more they are bent). On the other hand, the DES pulp fibers showed a higher coarseness value than the KP and sulfite pulp fibers, which may not necessarily have a positive effect on further products such as office paper, as this higher coarseness value may be due to the higher lignin content in the DES pulp fiber. Therefore, additional properties of DES pulp fibers and above all paper sheets made from these fibers should be investigated to better understand the strength of DES pulp and compare it to the values of the KP and sulfite pulp fibers and paper sheets made from them.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s13399-023-05156-y>.

**Acknowledgements** The authors thank Mondi AG Austria for the kraft pulp sample. Thanks to CTP, Mondi, and Sappi for fiber analysis. Thanks also go to Heribert Winter and Vincent Philippi (Sappi), Thomas Tripolt (Mondi), François Cottin, and Michel Petit-Conil (CTP) for the fiber analyses. Leo Arpa is acknowledged for his expert advice.

**Author contribution** Alan Perez: investigation, methodology, data analysis, writing—original draft.

Yagnaseni Roy: investigation, methodology, data analysis.

Constantijn Rip: investigation, methodology, data analysis, writing—review and editing.

Sascha R.A. Kersten: methodology, project administration, supervision.

Boelo Schuur: supervision, project administration, funding acquisition, writing—review and editing, methodology.

**Funding** This project received funding from TKI E&I with the supplementary grant “TKI-Toeslag” for Topconsortia for Knowledge and Innovation (TKI’s) of the Dutch Ministry of Economic Affairs and Climate Policy. The authors would like to thank the members of the ISPT “Deep Eutectic Solvents in the pulp and paper industry” consortium for their financial and in kind contributions. This cluster consists of the following organizations: BASF, CTP, CTS Twente, ISPT, Mayr-Melnhof Karton, Mid Sweden University, Mondi, Sappi, Stora Enso, University of Aveiro, University of Twente, Valmet Technologies Oy, VTT Technical Research Centre of Finland Ltd, WEPA, and Zellstoff Pöls. More information about the project can be found at <https://ispt.eu/projects/deep-eutectic-solvents>.

**Data availability** Data reported in the manuscript can be requested at the corresponding author.

## Declarations

**Ethical approval** Not applicable.

**Competing interests** The authors declare no competing interests.

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